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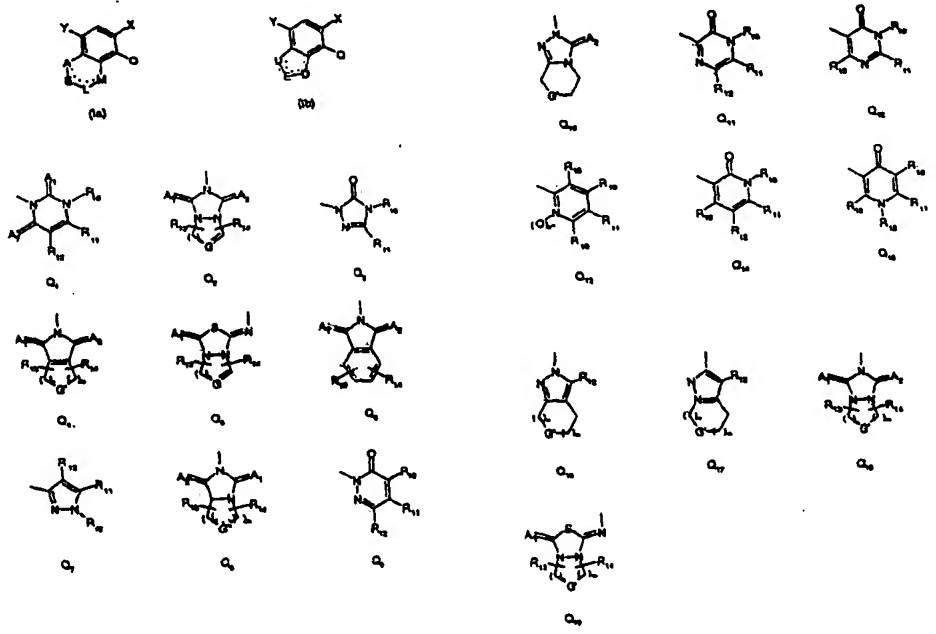
(54) Title: FUSED–BENZENE DERIVATIVES USEFUL AS HERBICIDES



(57) Abstract

This invention relates to fused–benzene derivatives, their salts and compositions, intermediates, a process of producing them and their use as herbicides.

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FUSED-BENZENE DERIVATIVES USEFUL AS HERBICIDES

BACKGROUND OF THE INVENTION

Field of the Invention

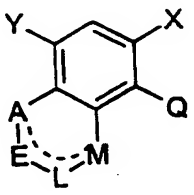
The present invention relates to novel fused-benzene derivatives, their salts and compositions, intermediates, a process for producing them, and their use as herbicides.

Description of the Related Art

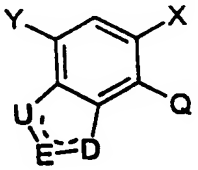
U.S. 4,859,229 discloses the herbicidal utility of uracil derivatives, in which the phenyl ring of the described compounds did not have any 2,6-disubsutitutions. Recently WO98/38188 and WO99/31091 disclosed benzoxazole and benzothiazole derivatives which have potent herbicidal activity in preemergence and postemergence applications.

The formula is;

wherein;



(Ia')



(Ib')

Q is uracil and D is either oxygen or sulfur. U.S. 5,169,431 disclosed benzofuran or benzothiophene type derivatives with Q as uracil and D is carbon. WO97/29105 disclosed benzofuran derivatives with Q as uracil and D is oxygen. WO93/14073 disclosed substituted dihydrobenzofuran type compounds with Q as uracil or triazine derivatives and D is carbon. U.S. 5,521,147 disclosed dihydrobenzofuran, dihydrobenzopyran and dihydrobenzofuran-3-one type derivatives with Q as uracil and D or M is oxygen. EP. 0,271,170 disclosed dihydrobenzofuran and dihydrobenzopyran derivatives where Q is many kinds of heterocycles and D or M is carbon. WO95/33746 disclosed cyclic sulfonamide derivatives where Q is many kinds of heterocycles including uracil and D is carbon. U.S. 5,346,881 discl sed benzodi xin or benzodioxole derivatives where Q is uracil, M is oxygen. JP 09301973 disclosed 2H-chromene type derivatives with Q is many kinds of heterocycles including uracil and M is oxygen. WO97/12886 disclosed benzisoxazole or

benzisoxazolidinone derivatives where Q is many kinds of heterocycles including uracil and D is oxygen.

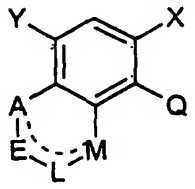
WO97/42188 disclosed indole type derivatives with Q as uracil and D or U isnitrogen.

Despite the broad coverage of these patents, the general structure of the present invention has not been described.

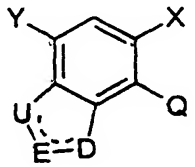
The specific fused-benzene compounds of the formula (Ia) and (Ib) mentioned below are novel and can be used to effectively control a variety of broad or grassy leaf plant species.

SUMMARY OF THE INVENTION

The invention delineates a method for the control of undesired vegetation in a plantation crop by the application to the locus of the crop an effective amount of a compound described herein. The present application describes certain herbicidal fused benzene derivatives of the formula (Ia) and (Ib) including all geometric, tautomeric and stereo isomers, and their salts, as well as compositions containing them and methods of preparation for these compounds.



(Ia)



(Ib)

in which

X, Y are independent of each other and are represented by hydrogen, halogen, cyano, nitro, (C_{1-4})alkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkyl or (C_{1-4})haloalkoxy;

A is oxygen, nitrogen, NR_1, CR_3, CR_3R_4, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_1)$;

D is nitrogen or NR_2;

M is CR_5, CR_5R_6, nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

When A is oxygen, M is nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

E and L are independent of each other and may be selected from CR_7, CR_8, CR_7R_8, oxygen, nitrogen, NR_7, $S(O)_{n*}$, C(=O), C(=S), $C(=NR_7)$ or CNR_7R_8;

U is CR_9, oxygen, nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

When U is CR_9, E is nitrogen;

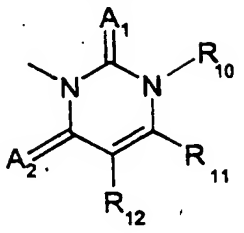
R_1 and R_2 are independent of each other and may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{2-6})alkenyl, (C_{2-6})alkynyl, (C_{1-6})alkylcarbonyl, (C_{-6})cycloalkylcarbonyl, (C_{1-6})haloalkylcarbonyl, (C_{1-6})alkoxycarbonyl, arylcarbonyl and heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

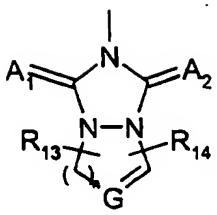
R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, nitro, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, (C_{3-6})cyclocarbonyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-6})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be optionally substituted with one or one more of the following group consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxy, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, haloaryl, alkoxyaryl, aryoxy, arylthio, haloaryloxy, heteroaryl, heteroaryloxy and (C_{3-7})cycloalkyl;

n* is represent an integer from 0 to 2;

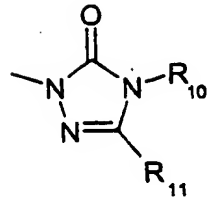
Q is selected from;



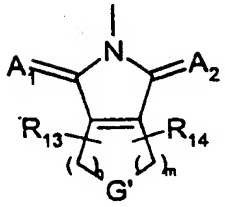
Q_1



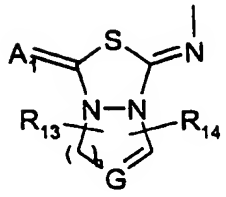
Q_2



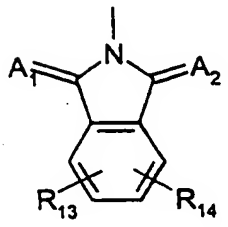
Q_3



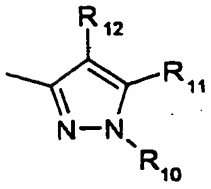
Q_4



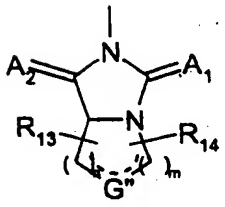
Q_5



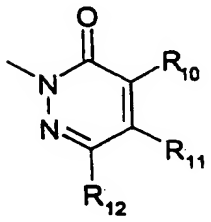
Q_6



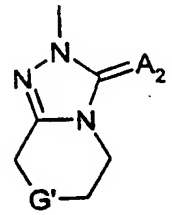
Q_7



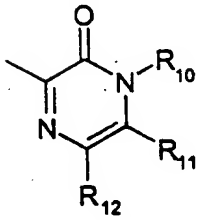
Q_8



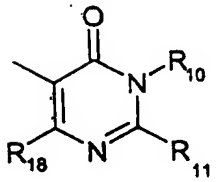
Q_9



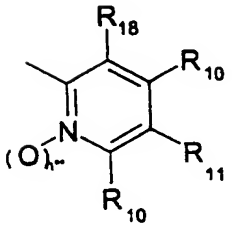
Q_{10}



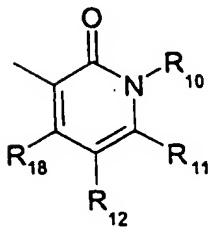
Q_{11}



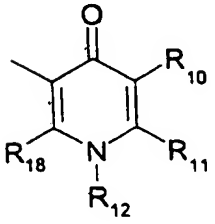
Q_{12}



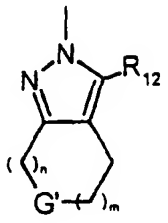
Q_{13}



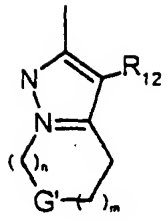
Q_{14}



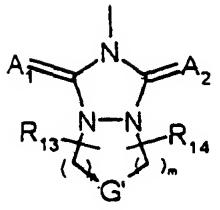
Q_{15}



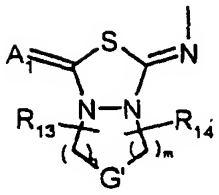
Q_{16}



Q_{17}



Q_{18}



Q_{19}

wherein

A_1 and A_2 are independently oxygen or sulfur;

R_{10} is hydrogen, halogen, cyano, nitro, formyl, (C_{1-4})alkyl, (C_{1-4})haloalkyl, amino, (C_{1-4})alkylamino, (C_{1-4})haloalkylamino, (C_{1-4})alkoxyamino, (C_{1-4})haloalkoxyamino, (C_{1-4})alkylcarbonyl, (C_{1-4})haloalkylcarbonyl, (C_{1-4})haloalkoxycarbonyl, (C_{1-4})alkylcabonylamino, (C_{1-4})haloalkylcarbonylamino, (C_{1-4})alkoxycarbonylamino, (C_{1-4})haloalkoxycarbonylamino, (C_{1-6})alkoxyalkyl, (C_{1-6})haloalkoxyalkyl, (C_{1-6})alkylthio, (C_{1-6})haloalkylthio, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, (C_{2-6})alkynyl or (C_{2-6})haloalkynyl;

R_{11}, R_{12} and R_{18} are independent of each other and may be selected from the group consisting of hydrogen, halogen, cyano, (C_{1-4})alkyl, (C_{1-4})haloalkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkoxy, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, hydroxy or amino which may be optionally substituted with (C_{1-4})alkyl and (C_{1-4})haloalkyl;

R_{13} and R_{14} are independent of each other and may be selected from the group consisting of hydrogen, halogen, (C_{1-3})alkyl, (C_{1-3})haloalkyl, hydroxy, (C_{1-3})alkoxy, (C_{1-3})haloalkoxy, cyano, nitro, amino or (C_{1-6})alkylamino;

When R_{13} and R_{14} are taken together with the atoms to which they are attached, they represent a three to seven membered substituted or unsubstituted ring optionally containing oxygen, $S(O)_n$··· or nitrogen with following optional substitutions, one to

three halogen, cyano, nitro, hydroxy, amino, carbonyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl or (C_{3-7})cycloalkyl;

G is nitrogen or CR_{16};

G' is NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$;

G'' is nitrogen, CR_{16}, NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$

R_{15} may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl; where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

R_{16} and R_{17} are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, (C_{3-6})cyclocarbonyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be optionally substituted with one or one more of the following group consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})

$_6$)haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

n and m are independent of each other and represent an integer from 0 to 2; provided that m+n is 2, 3 or 4;

n** is 0 or 1;

n*** is represent an integer from 0 to 2;

When Q is Q_1, Q_3, Q_4, Q_{13}, Q_{18} or Q_{19}, structure (Ib) is excluded;

When Q is Q_7, U is CR_9, nitrogen, NR_2, C(=O), C(=S) or C(=NR_2);

Preferred compounds for the reasons of greater herbicidal efficacy are represented by formula (Ia) and (Ib) where

X, Y are independent of each other and are represented by hydrogen, halogen or cyano;

A is oxygen, nitrogen, NR_1;

D is nitrogen or NR_2;

M is nitrogen or NR_2;

E and L are independent of each other and may be selected from CR_7, CR_8, CR_7R_8, oxygen, nitrogen, $S(O)_{n*}$, C(=O), C(=S), C(=NR_7) or CNR_7R_8;

U is oxygen, nitrogen, NR_2 or $S(O)_{n*}$;

R_1 and R_2 are independently of each other and may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{2-6})alkenyl, (C_{2-6})alkynyl, (C_{1-6})alkylcarbonyl, (C_{-6})cycloalkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, haloaryl,alkoxyaryl,heteroaryl and (C_{3-7})cycloalkyl;

R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_1-

$_6$)alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, aryloxy, heteroaryl heteroaryloxy and (C_{3-7})cycloalkyl;

n* is represent an integer from 0 to 2;

When Q is Q_1 or Q_3 structure (Ib) is excluded;

When Q is Q_7, U is nitrogen or NR_2;

Q is selected from Q_1, Q_2, Q_3, Q_7, Q_9, Q_{10}, Q_{16} or Q_{17};

wherein

A_1 and A_2 are independently oxygen or sulfur;

R_{10} is (C_{1-3})alkyl, (C_{1-3})haloalkyl or amino

R_{11}, R_{12} are independent of each other and may be selected fron the group consisting of hydrogen, halogen, cyano, (C_{1-4})alkyl, (C_{1-4})haloalkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkoxy, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, hydroxy or amino which may be substituted with (C_{1-4})alkyl or (C_{1-4})haloalkyl;

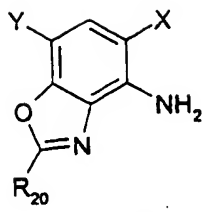
R_{13} and R_{14} are independently of each other and may be selected from the group consisting of hydrogen, halogen, (C_{1-3})alkyl, (C_{1-3})haloalkyl, hydroxy, (C_{1-3})alkoxy, (C_{1-3})haloalkoxy, cyano, nitro, amino and (C_{1-6})alkylamino;

G is nitrogen or CR_{16},;

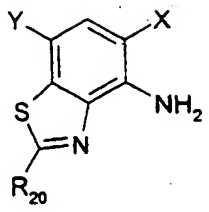
G' is NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$;

R_{15} may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl;
R_{16} and R_{17} are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;
n and m are independent of each other and represent an integer from 0 to 2; provided that m+n=2 or 3;
n** is 0 or 1;
n*** is represent an integer from 0 to 2;

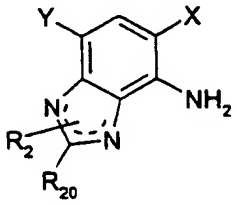
Certain compounds of present invention are novel. These are represented by the following formula:



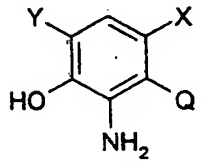
a



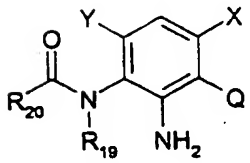
b



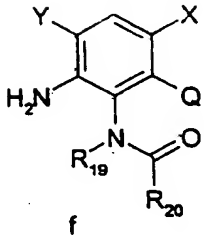
c



d



e



f

in which

X is hydrogen or halogen;

Y is halogen, cyano, nitro, (C_{1-3})haloalkyl, or (C_{1-3})alkoxyalkyl;

Q is O_1, Q_2, Q_3, Q_7, Q_9, Q_{10}, Q_{16} or Q_{17};

R_{19} is hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl, heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

R_{20} is selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy, (C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl, (C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy,

(C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-6})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

In the definitions given above, unless alkyl, alkenyl and halogen are defined or mentioned, the term alkyl used either alone or in compound words such as "haloalkyl" or "alkylcarbonyl" includes straight-chain or branched chains containing 1 to 6 carbon atoms. The terms of alkenyl and alkynyl include straight chain or branched alkenes and alkynes respectively containing 2 to 6 carbon atoms, and the term halogen either alone or in the compound words such as haloalkyl indicates fluorine, chlorine, bromine, or iodine. Further a haloalkyl is represented by an alkyl partially or fully substituted with halogen atoms which may be same or different. The term or part of the term "aryl" or "heteroaryl" are defined as those monocyclic or fused bicyclic aromatic rings wherein at least one ring satisfy the Hückel rule and contain 0 to 4 heteroatoms, examples include: phenyl, furyl, furazanyl, thienyl, pyrrolyl, pyrazolyl, oxazolyl, oxadiazolyl, imidazolyl, isoxazolyl, thiazolyl, thiadiazolyl, isothiazolyl, tetrazolyl, pyridinyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, quinolyl, isoquinolyl, quinoxalinyl, benzofuranyl, 2,3-dihydrobenzofuranyl, isobenzofuranyl, benzothienyl, benzodioxolyl, chromanyl, indolinyl, isoindolyl, naphthyl, thienofuranyl and purinyl. These rings can attached through any available carbon or nitrogen, for example, when the aromatic ring system is furyl, it can be 2-furyl or 3-furyl, for pyrrolyl, the aromatic ring system is 1-pyrrolyl, 2-pyrrolyl or 3-pyrrolyl, for naphthyl, the carbobicyclic aromatic

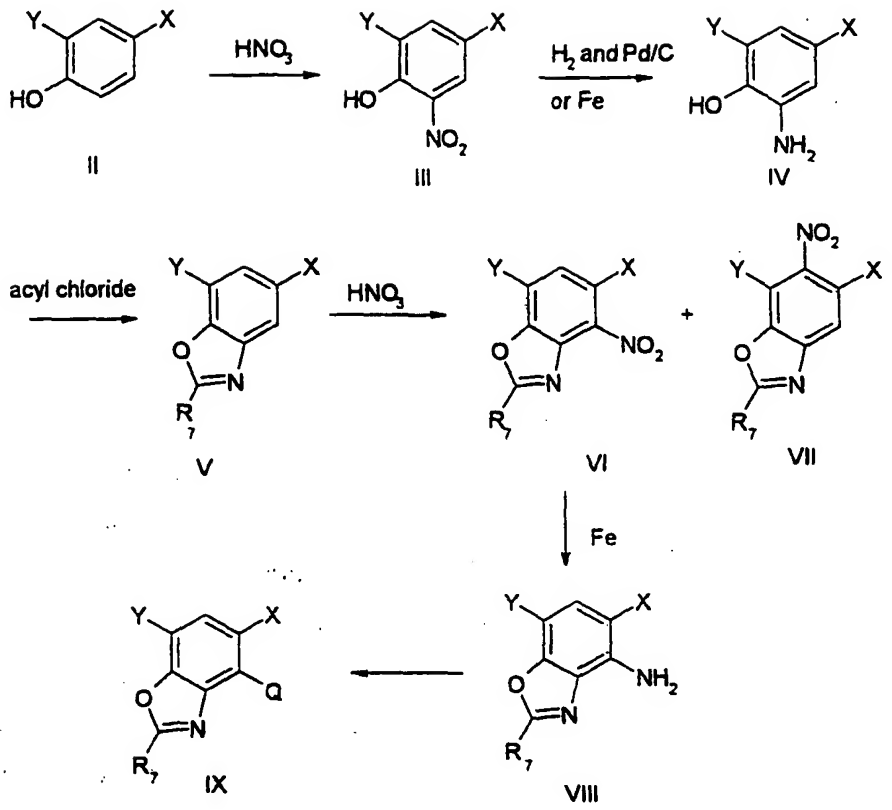
ring is 1-naphthyl or 2- naphthyl and for benzofuranyl, the aromatic ring system can be 2-, 3-, 4-, 5-, 6- or 7-benzofuranyl.

DETAILED DESCRIPTION OF THE INVENTION

The compounds described by the Formula (Ia) and (Ib) can be prepared by the procedures as described herein. Using commercially available starting materials or those whose synthesis is known in the art, the compounds of this invention may be prepared using methods described in the following Schemes, or using modifications thereof which are within the scope of the art. The starting phenol represented by formula II in Scheme 1 can be nitrated according to the literature procedure (WO 9722618). The reaction is accomplished by treatment with nitric acid at a temperature between -30°C and 50°C for 0.5-12 hours. The reaction solution is poured into ice-water, then isolated and purified. IV can be prepared by the reduction of III typically by treatment with iron in an acidic medium such as acetic acid or catalytic hydrogenation at a temperature between 0°C and 50°C for 1-24 hours. IV can be treated with acid chloride or acid anhydride in the presence of base such as trimethyl amine or acid such as pyridinium *p*-toluensulfonate (PPTS) in an inert solvent such as *m*-xylene at 20-250°C for 1-24 hours to give benzoxazole type compound represented by formula V. These compounds can be nitrated with a nitration reagent such as nitric acid at a temperature between -10°C and 50°C for 0.5-12 hours. The reaction solution is poured into ice-water followed by filtration. VI can be obtained as a mixture with its regio-isomer represented by formula VII.

The reduction of VI to amine derivatives represented by formula VIII can be carried out by treatment with iron in an acidic medium such as acetic acid or by catalytic hydrogenation at a temperature between 0°C and 30°C for 1-24 hours. Further modification from VIII to IX can be carried out as described in this patent.

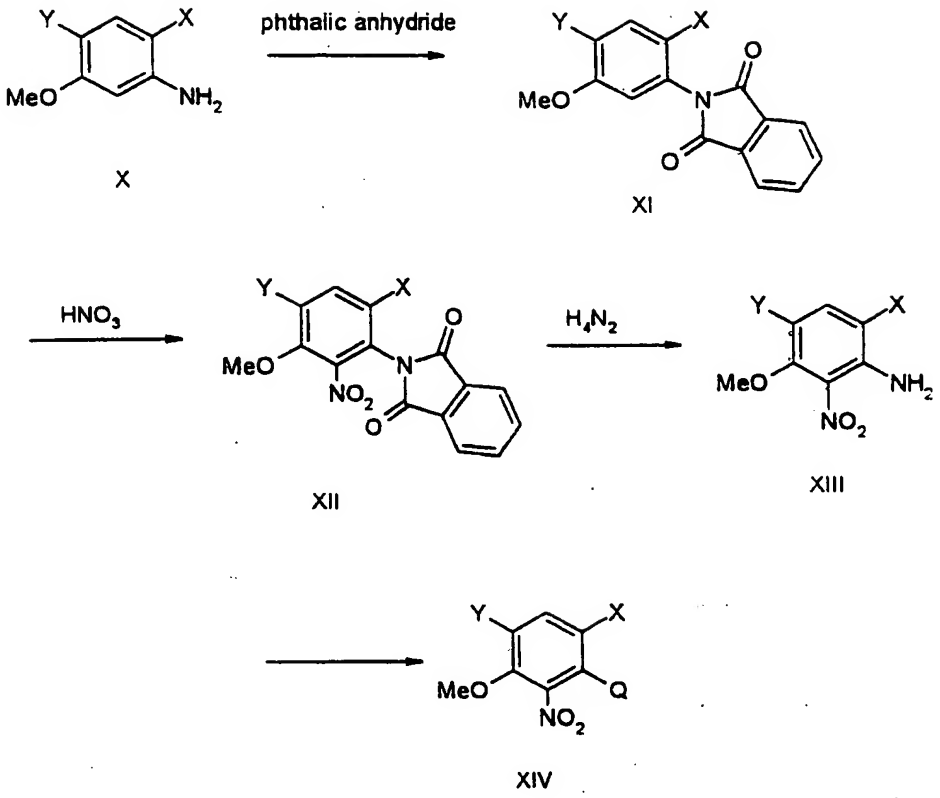
SCHEME 1



The phthalimide derivative represented by formula XI can be prepared by the treatment of X with phthalic anhydride in an acidic medium such as acetic acid at a temperature between 30°C and 200°C for 1-24 hours.

Nitration can be carried out by its addition to a mixture of sulfuric acid and nitric acid at a temperature between -15°C and 50°C for 0.5-12 hours followed by addition of ice-water to give the desired compound represented by formula XII. XII can be deprotected to give amine derivatives represented by formula XIII. Removal of the protecting group can be accomplished using several methods such as treatment with hydrazine in a polar solvent such as dimethylsulfoxide (DMSO) or by treatment with an organic amine such as methyl amine in ethanol. Amino group of XIII can be derived to XIV as described in this patent.

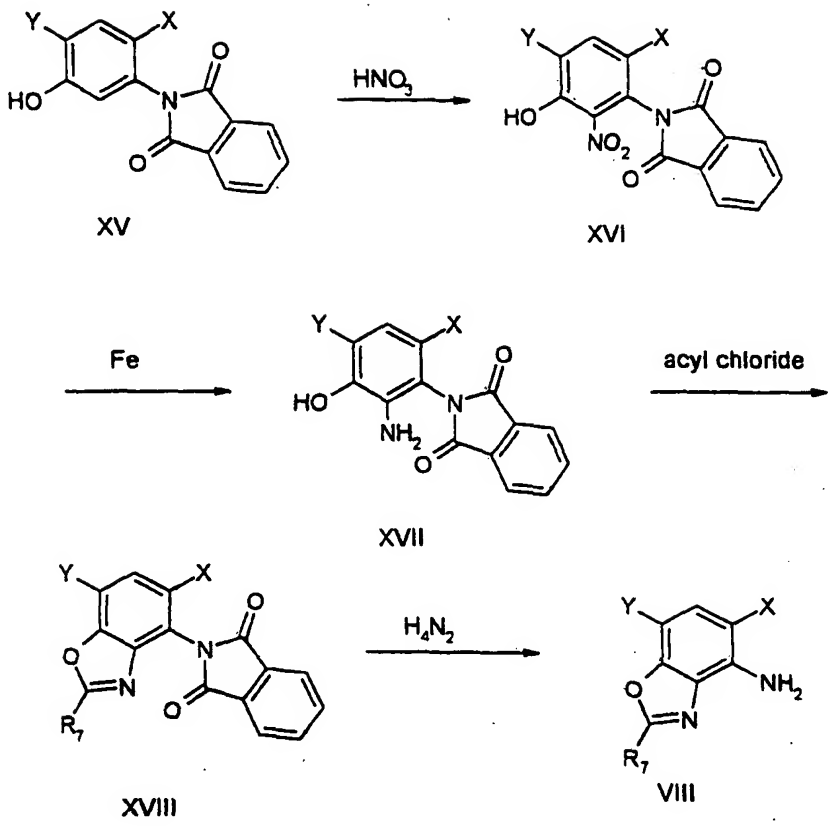
SCHEME 2



X XI XII XIII XIV

Phthalimide derivative represented by the formula XV in Scheme 3 can be prepared according to the literature procedure (WO 93/14073). Nitration can be carried out by treatment with a nitrating reagent such as nitric acid at a temperature between -30°C and 30°C for 0.5-12 hours. XVI is then converted into the corresponding amine represented by formula XVII by typical reduction procedures e.g. iron in an acidic medium such as acetic acid or by catalytic hydrogenation. Benzoxazole derivatives represented by formula XVIII can be prepared according to the general procedures described in Scheme 1. The phthalimide group can be removed according to the general procedure described in Scheme 2 to give VIII.

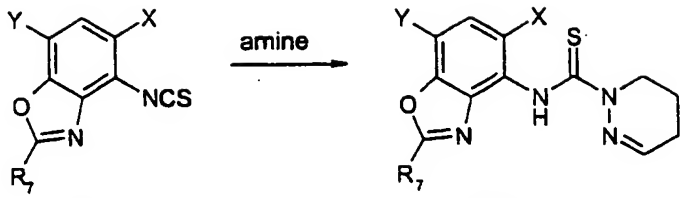
SCHEME 3



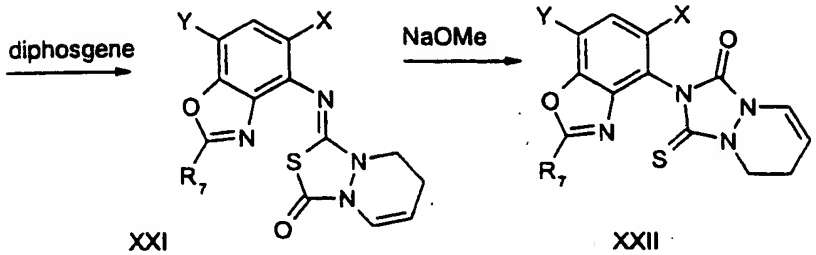
XV XVI XVII XVIII VIII

The product represented by formula XXII in Scheme 4 can be prepared analogously by known method (JP2-289573). Urea derivatives represented by formula XX can be prepared by a coupling reaction with the corresponding amine in an inert solvent such as ethyl acetate at a temperature between 0°C and 30°C for 1-12 hours. XXI can be prepared from XX by using diphosgene or related reagent such as triphosgene in an inert solvent such as dichloromethane at a temperature between 0°C and 150°C for 1-12 hours. The final compounds represented by formula XXII can be prepared from XXI by treatment with a catalytic amount of base such as sodium methoxide in a polar solvent such as methanol at a temperature between 20°C and 150°C for 0.5-12 hours.

SCHEME 4



XIX XX

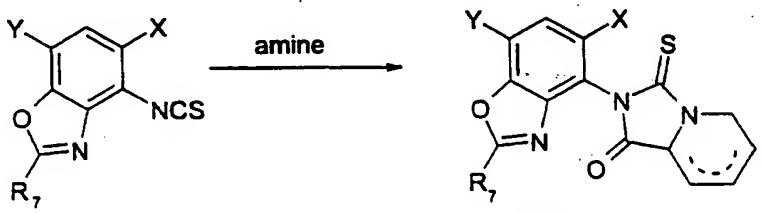


XXI XXII

The product represented by the formula XXIII in Scheme 5 can be prepared analogously by known method (EP 688773).

The reaction is carried out at a temperature between -78°C and 100°C for 0.5-24 hours in an inert solvent such as tetrahydrofuran (THF) or toluene.

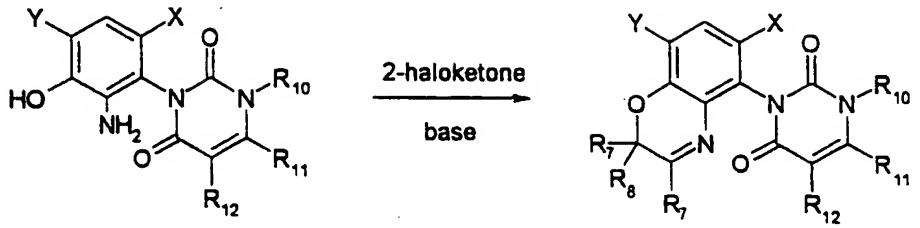
SCHEME 5



XIX XXIII

The compounds represented by formula XXV in Scheme 6 can be prepared from XXIV by treatment with 2-halo keto-derivatives such as phenacyl bromide in the presence of base such as potassium carbonate in an inert solvent such as acetone or acetonitrile. The reaction can be carried out at a temperature between 30°C and 100°C for 1-24 hours.

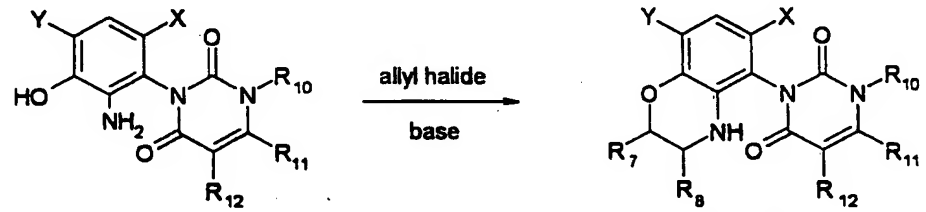
SCHEME 6



XXIV XXV

The compounds represented by formula XXVI in Scheme 7 can be prepared according to the procedure outlined by Y. Masuoka et al. in Chem Pharm. Bull 34(1) 130-139 (1986). The starting compound represented by formula XXIV was treated with allyl halide such as methyl 4-bromocrotonate in the presence of base such as sodium bicarbonate in a solvent such as methanol at a temperature between 0°C and 100°C for 1-24 hours

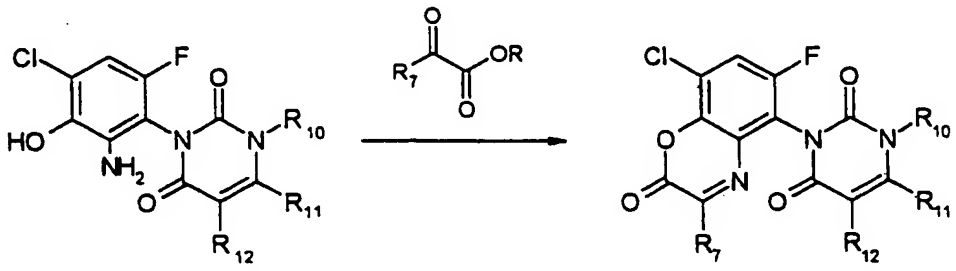
SCHEME 7



XXIV XXVI

The product represented by formula XXVII in Scheme 8 can be prepared from XXIV by treatment with 1,2-dicarbonyl derivatives such as methyl pyruvate in an inert solvent such as toluene or THF. The reaction carried out at a temperature between 0°C and 150°C for 0.5-24 hours.

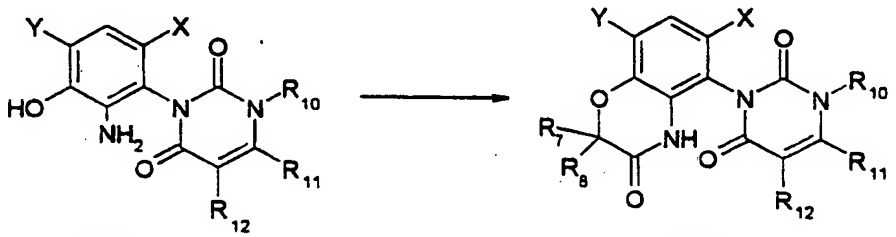
SCHEME 8



XXIV XXVII

The product represented by formula XXVIII in Scheme 9 can be prepared from XXIV by a cyclization reaction with 2-halogenated ester such as ethyl 2-bromopropionate. The reaction can be carried out in the presence of base such as potassium carbonate in a solvent such as acetonitrile at a temperature between 25°C and 100°C for 1-24 hours.

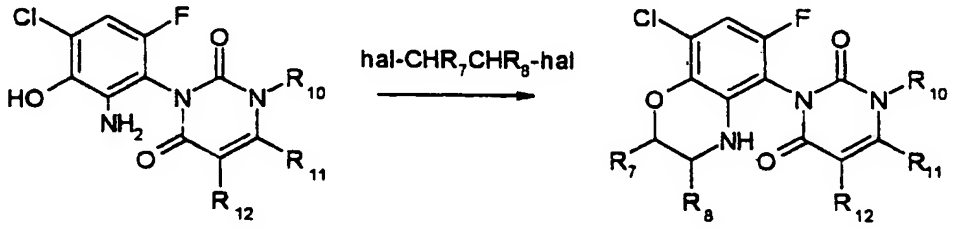
SCHEME 9



XXIV XXVIII

The compounds represented by formula XXVI in Scheme 10 can be prepared from XXIV using 1,2-dihaloderivatives such as 1,2-dibromoethane in the presence of base such as potassium carbonate in an inert solvent such as acetone.
The reaction is carried out at a temperature between 20°C and 150°C for 0.5-24 hours.

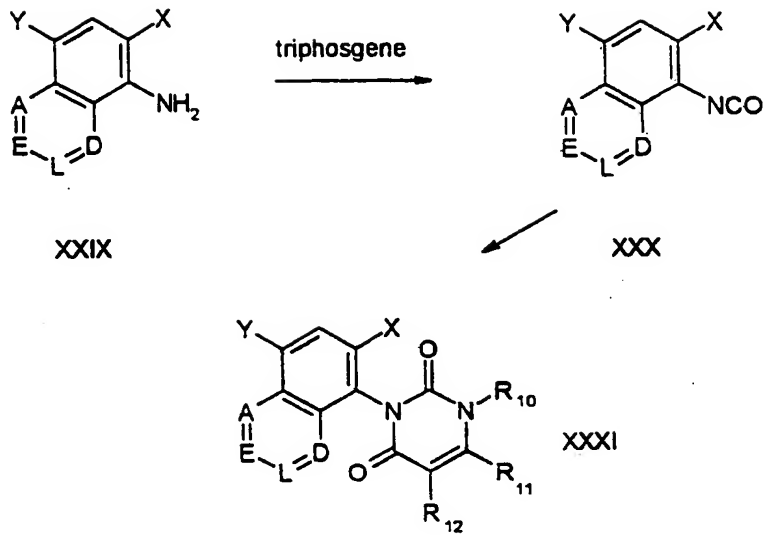
SCHEME 10



XXIV XXVI

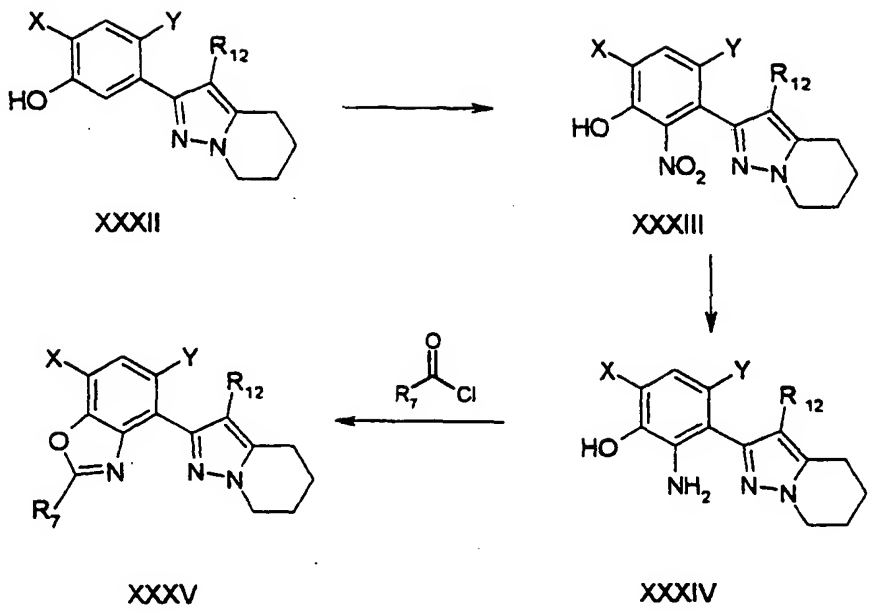
Aniline derivatives represented by formula XXIX in Scheme 11 can be converted to corresponding isocyanates represented by formula XXX, using phosgene or triphosgene in the presence of base such as triethylamine. The reaction can be carried out in an inert solvent such as ethyl acetate at a temperature between 0°C and 100°C for 0.5-24 hours.
Uracil derivatives represented by formula XXXI can be prepared analogously by known method (U.S. 4,859,229).

SCHEME 11



The starting pyrazole derivatives represented by formula XXXII in Scheme 12 can be nitrated with a nitrating reagent such as nitric acid in an acidic medium such as sulfuric acid at a temperature between -30°C and 50°C for 0.5-12 hours. Product (XXXIII) is isolated by addition of water and filtered. XXXIV can be prepared by the reduction of XXXIII typically by catalytic hydrogenation in the presence of catalysts such as palladium on carbon or by treatment with iron in an acidic medium such as acetic acid. Further modification of XXXIV to XXXV is carried out according to the general procedures described in Scheme 1.

SCHEME 12

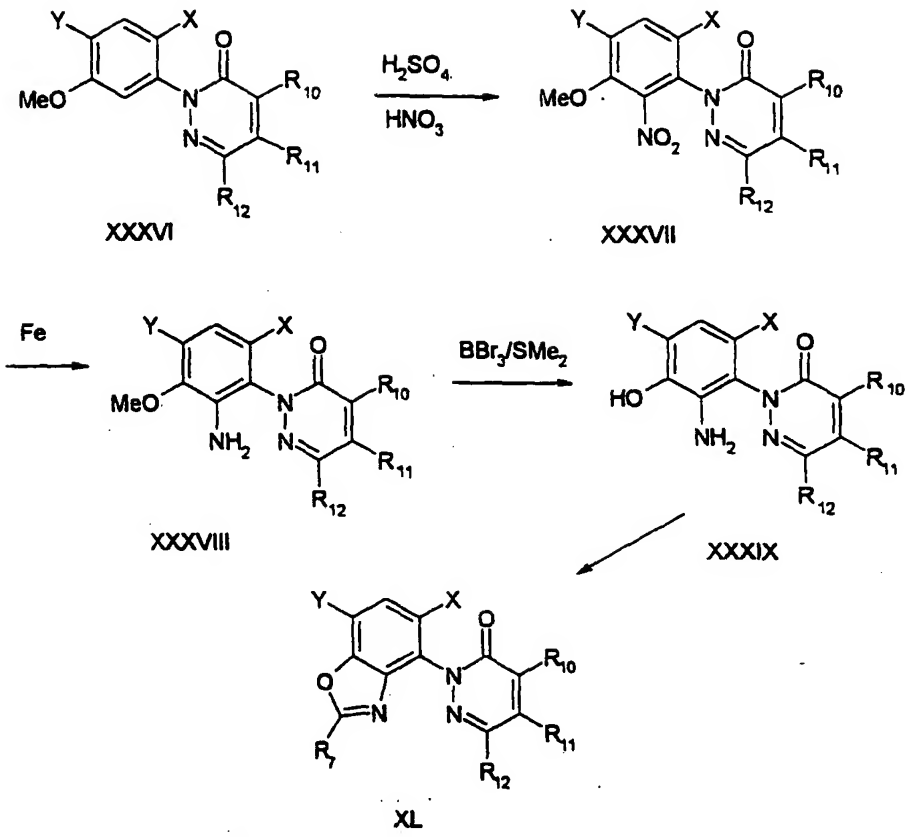


XXXII XXXIII

XXXV XXXIV

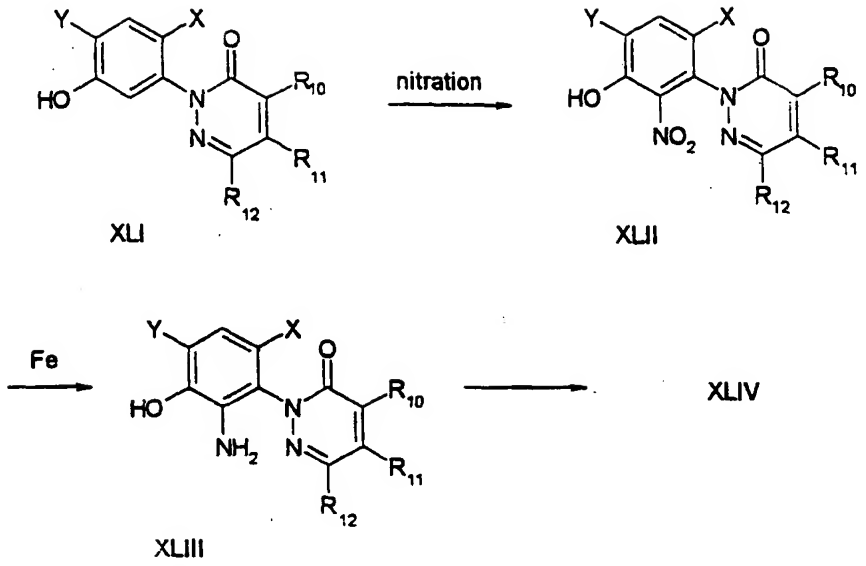
The starting compounds represented by formula XXXVI in Scheme 13 can be prepared analogously by known method (WO97/07104). Nitration can be carried out with a nitrating reagent such as nitric acid in an acidic medium such as sulfuric acid at a temperature between -30°C and 50°C for 0.5-12 hours to give XXXVII. Aniline derivatives represented by formula XXXVIII can be prepared from XXXVII by treatment with iron in an acidic medium such as acetic acid or by catalytic hydrogenation. Further transformation through aminophenol represented by formula XXXIX to XL can be carried out following to the method described in Scheme 1.

SCHEME 13



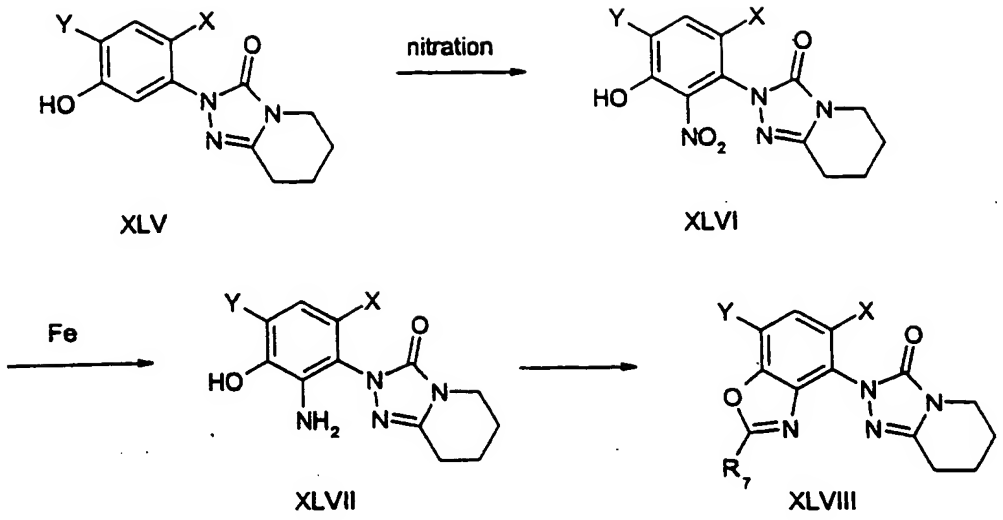
The starting compounds represented by formula XLI in Scheme 14 can be prepared according to the literature procedure (WO97/07104). Nitration can be carried out with a nitrating reagent such as nitric acid. The reaction can be carried out at a temperature between -20°C and 100°C for 0.5-12 hours to give XLII. Aniline derivative represented by formula XLIII can be prepared from XLII by treatment with iron in an acetic medium such as acetic acid or by catalytic hydrogenation. Further transformation through aminophenol represented by formula XLIII to XLIV can be carried out following to the method described in Scheme 1.

SCHEME 14



The starting compound represented by formula XLV in Scheme 15 can be prepared following literature methods, such as US patent 4,213,773. Nitration can be carried out with a nitrating reagent such as nitric acid with or without acidic medium such as sulfuric acid at a temparature between -20°C and 50°C for 0.5-24 hours to give XLVI. Aminophenol derivatives represented by formula XLVII can be prepared from XLVI by treatment with iron in an acidic medium such as acetic acid or by catalytic hydrogenation. The reaction can be carried out at a temperature between 0°C and 100°C for 1-48 hours. Benzoxazole derivatives represented by formula XLVIII can be prepared according to the general procedures described in Scheme 1.

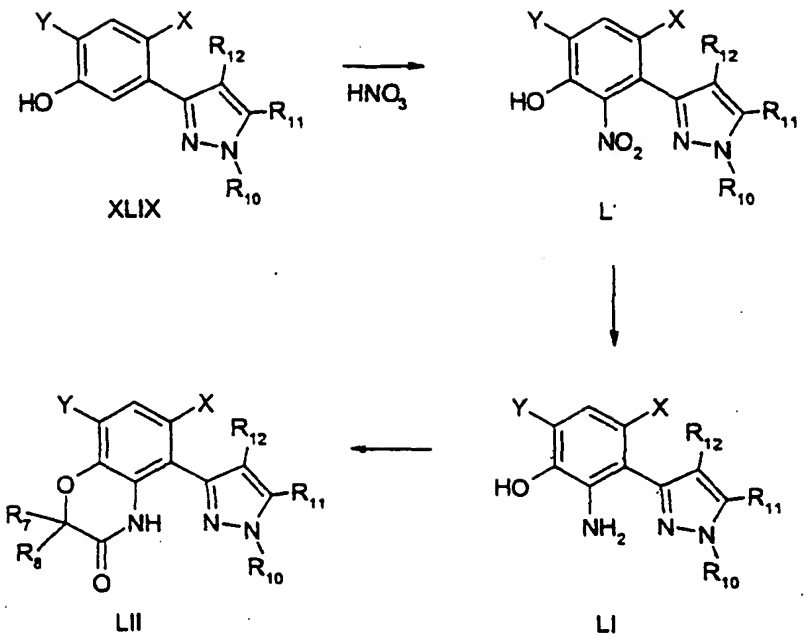
SCHEME 15



XLV XLVI XLVII XLVIII

The starting compound represented by formula XLIX in Scheme 16 can be prepared following literature method (WO92/06962). Nitration can be carried out with a nitrating reagent such as nitric acid with or without acidic medium such as sulfuric acid at a temperature between –20°C and 50°C for 0.5-24 hours to give L. Aminophenol derivatives represented by formula LI can be prepared from L by treatment with iron in an acidic medium such as glacial acetic acid or by catalytic hydrogenation in the presence of catalyst such as palladium on carbon. The reaction can be carried out at a temperature between 0°C and 100°C for 1-48 hours. Further modification of LI to LII is carried out according to the general procedures described in Scheme 9.

SCHEME 16



EXAMPLE 1

Preparation of 4-amino-7-chloro-2-ethyl-5-fluorobenzoxazole (Compound no. 14-3)

Step 1 Preparation of 2-chloro-4-fluoro-6-nitrophenol as an intermediate.

2-Choro-4-fluorophenol (24g) was slowly added to nitric acid (69%, 100ml) at 0°C. The mixture was stirred for 20 minutes and then poured into ice-water (250 ml), the resulting yellow crystals were separated by filtration and washed with cold water, and dried in vacuum to afford the title compound (29g). ^{1}H-NMR ($CDCl_3$, 300MHz): 7.53(1H, dd, J=3.0Hz, 7.2Hz), 7.79(1H, dd, J=3.1Hz, 8.0Hz), 10.78(1H, s) ppm.

Step 2 Preparation of 2-amino-6-chloro-4-fluorophenol as an intermediate.

2-Chloro-4-fluoro-6-nitrophenol (13.5g) was dissolved in ethyl acetate (150ml) containing palladium on activated carbon (10%, 1.35g). The hydrogen was bubbled through the suspension for 16 hours. and the mixture was filtered. After evaporation of the solvent, the title compound was obtained as white crystals (10.4g). ^{1}H-NMR ($CDCl_3$, 300MHz): 3.99(2H, br s), 5.28(1H, br s), 6.37(1H, dd, J=2.9Hz, 9.8Hz), 6.47(1H, dd, J=2.9Hz, 8.3Hz) ppm.

Step 3 Preparation of 7-chloro-2-ethyl-5-fluorobenzoxazole as an intermediate

2-Amino-6-chloro-4-fluorophenol (3g) was dissolved in m-xylene (150ml) containing propionyl chloride (2.05g), triethylamine (2.24g) and pyridinium p-toluenesulfonate (2.8g). The mixture was refluxed under N_2 for 4 hours, then cooled to room temperature and passed through a silica gel column eluted with a mixture of hexane and ether (5:1) to yield the title compound as a pale-brown solid (2.85g). ^{1}H-NMR ($CDCl_3$, 300MHz): 1.45(3H, t, J=7.6Hz), 2.98(2H, q, J=7.6Hz), 7.07(1H, dd, J=2.3Hz, 9.2Hz), 7.27(1H, dd, J=2.4Hz, 8.1Hz) ppm.

Step 4 Preparation of 7-chloro-2-ethyl-5-fluoro-4-nitrobenzoxazole as an intermediate

7-Chloro-2-ethyl-5-fluorobenzoxazole (0.9g) was slowly added to a mixture of sulfuric acid (9ml) and nitric acid (0.6ml) at -40°C. The dryice-acetone bath was removed and the mixture stirred for 2 hours. Ice-water was added and the mixture was extracted with ether. The organic phase was dried over anhydrous sodium sulfate and concentrated to an oil under reduced pressure. The residue was purified by column chromatography on silica gel using 5% ether in hexane. The desired product was obtained as a white solid [0.35g, ^{1}H-NMR ($CDCl_3$, 300MHz): 1.48(3H, t, J=7.6Hz), 3.07(2H, q, J=7.6Hz), 7.27(1H, d, J=10.5Hz) ppm], along with a by-product, 7-chloro-2-ethyl-5-fluoro-6-nitrobenzoxazole (0.49g).

Step 5 Palladium on activated carbon (10%, 0.1g)was added to a solution of 7-chloro-2-ethyl-5-fluoro-4-nitrobenzoxazole (0.86g) in ethyl acetate (80ml) and hydrogen was bubbled through the suspension for 5 hours. After filtration and evaporation, 4-amino-7-chloro-2-ethyl-5-fluorobenzoxazole(0.73g) was obtained as the single product.

EXAMPLE 2

Preparation of N-(2-*t*-butyl -7-chloro-5-fluorobenzoxazol-4-yl)phthalimide (Compound no. 6-2)

Step 1 Preparation of N-(4-chloro-2-fluoro-5-hydroxyphenyl)phthalimide as an intermediate

5-Amino-2-chloro-4-fluorophenol (3.0 g) and phthalic anhydride (2.75 g) were dissolved in acetic acid (60 ml) and the solution was refluxed for 2 hours. After allowing it to cool to ambient temperature, the solution was added to water and the precipitate was separated by filtration to furnish the title compound (5.04 g). ^{1}H NMR ($CDCl_3$+CD_3OD, 300

MHz) 3.68 (1H, s), 6.93 (1H, d, J=6.6 Hz), 7.27 (1H, d, J=9.1 Hz), 7.84 (2H, dd, J=3.0, 5.5 Hz), 7.97 (2H, dd, J=3.0, 5.5 Hz) ppm.

Step 2 Preparation of N-(4-chloro-6-fluoro-3-hydroxy-2-nitrophenyl)phthalimide as an intermediate

Powdered N-(4-chloro-2-fluoro-5-hydroxyphenyl)phthalimide (5.0 g) was slowly added to stirred HNO_3 (69%) at -10 °C. The solution was slowly warmed to room temperature and allowed to stir for 0.5 hour. The solution was then added to ice water and resultant precipitate was separated by filtration to afford the title compound (5.5 g). ^{1}H NMR ($CDCl_3$+CD_3OD, 300 MHz) 4.36 (1H, br s), 7.61 (1H, d, J=8.6 Hz), 7.88 (2H, dd, J=3.0, 5.5 Hz), 7.99 (2H, dd, J=3.0, 5.5 Hz) ppm.

Step 3 Preparation of N-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)phthalimide as an intermediate

N-(4-Chloro-6-fluoro-3-hydroxy-2-nitrophenyl)phthalimide (5.5 g) was dissolved in glacial acetic acid (55 ml) and iron powder (3.64 g) was slowly added. The solution was stirred at ambient temperature overnight. Water was added and the product extracted with ethyl acetate. The organic layer was washed with saturated sodium bicarbonate solution followed by water. Solvent was removed under reduced pressure to afford the title compound (4.86 g). ^{1}H NMR ($CDCl_3$, 300 MHz) 5.42 (1H, br s), 6.58 (1H, d, J=9.4 Hz), 7.95 (4H, m) ppm.

Step 4 Preparation of N-(2-*t*-butyl -7-chloro-5-fluorobenzoxazol-4-yl)phthalimide as an intermediate

A solution of N-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)phthalimide (2 g), triethylamine (0.79 g), pyridinium p-toluenesulfonate (0.99 g), and pivaloyl chloride (0.95 g) in m-xylene (65 ml) was refluxed for 8 hours. Solvent was then evaporated under reduced pressure and the product was subjected to silica gel chromatography. N-(2-*t*-butyl -7-chloro-5-fluorobenzoxazol-4-yl)phthalimide was eluted with methylene chloride as the eluent (2.17 g).

EXAMPLE 3

Preparation of 8-(7-chloro-2-ethyl -5-fluorobenzoxazol-4-yl)-1,6,8-triazabicyclo[4,3,0]2-nonene-9-one-7-thione (Compound no. 8-1)

Step 1 Preparation of 1-(7-chloro-2-ethyl-5-fluorobenzoxazol-4-yl-thiocarbamoyl)-1,4,5,6-tetrahydropyridazine as an intermediate

1,4,5,6-Tetrahydropyridazine (0.3g) and an equivalent of 7-chloro-2-ethyl-5-fluoro-4-isothiocyanobenzoxazole (preparation given in Example 15, Step1) were mixed in THF (30ml) and the mixture was stirred for 3 hours. Following evaporation of solvent, the residue was purified by column chromatography on silica gel using hexane-ethyl acetate (1:1) to afford 0.36g of the title compound. ^{1}H-NMR ($CDCl_3$, 300MHz): 1.42(3H, t, J=7.5Hz), 1.97(2H, m), 2.28(2H, m), 2.97(2H, q, J=7.6Hz), 4.36(2H, m), 7.01(1H, m), 7.16(1H, d, J=10.0Hz), 9.30(1H, s) ppm.

Step 2 Preparation of 9-(7-chloro-2-ethyl -5-fluorobenzoxazol-4-yl-imino)-8-thia-1,6-diazabicyclo[4,3,0]4-nonene-7-one as an intermediate

1-(7-Chloro-2-ethyl-5-fluorobenzoxazol-4-yl-thiocarbamoyl)-1,4,5,6-tetrahydropyridazine (0.33g) was dissolved in methylene chloride (5ml). The mixture was cooled in a dry ice/acetone bath (-20°C) and stirred during addition of pyridine (0.23g) and diphosgene (0.09ml). After removal of the cooling bath, the mixture was stirred for an additional 4 hours, followed by column chromatographic purification on silica gel using hexane-ethyl acetate (3:1) to give 0.2g of the title compound. ^{1}H-NMR ($CDCl_3$, 300MHz): 1.44(3H, t, J=7.5Hz), 2.54(2H, m), 2.98(2H, q, J=7.6Hz), 4.21(2H, t, J=5.8Hz), 5.36(1H, m), 6.93(1H, d, J=8.3Hz), 7.13(1H, d, J=10.6Hz) ppm.

Step 3 9-(7-Chloro-2-ethyl -5-fluorobenzoxazol-4-yl-imino)-8-thia-1,6-diazabicyclo[4,3,0]4-nonene-7-one (0.14g) was dissolved in methanol (10ml) containing sodium methoxide (0.03g). The mixture was refluxed for 0.5 hour. After evaporation of solvent, the residue was purified by passing through a silica gel column eluting by ether to give 8-(7-chloro-2-ethyl -5-fluorobenzoxazol-4-yl)-1,6,8-triazabicyclo[4,3,0]2-nonene-9-one-7-thione (0.14g).

EXAMPLE 4

Preparation of 8-(7-chloro-2-ethyl -5-fluorobenzoxazol-4-yl)-1,8-diazobicyclo[4,3,0]nonane-7-one-9-thione (Compounds no. 7-5 and 7-6)

Ethyl pipecolinate (0.51g) was mixed with an equivalent of 7-chloro-2-ethyl-5-fluoro-4-isothiocyanobenzoxazole (preparation given in Example 20, Step1) in ethyl acetate (25ml), and the resulting mixture stirred for 16 hours. After the solvent was evaporated, the residue was purified by column chromatography on silica gel using hexane-ethyl acetate (3:1) to give two diastereomers of the product (0.4g in total).

EXAMPLE 5

Preparation of 3-(8-chloro-6-fluoro-3-phenyl-2H-1,4-benzoxazin-5-yl) -1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 1-3)

A mixture of 3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione (0.5g), phenacyl bromide (0.29g) and potassium carbonate (0.2g) in acetone (30ml) was stirred under reflux conditions for 1hour. Then insoluble salt was removed through Celite and the filtrate concentrated under reduced pressure. The oily substance was purified by column chromatography on silica gel using ethyl acetate-hexane(1:4) as eluent to give the title compound (0.12g).

EXAMPLE 6

Preparation of 3-[8-chloro-6-fluoro-2-(methoxycarbonyl)methyl-3,4-dihydro -2H-1,4-benzoxazin-5-yl] -1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 2-8)

A mixture of 3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione (0.43g), methyl 4-bromocrotonate (0.22g) and sodium bicarbonate (0.3g) in methanol was stirred at 25°C for 12 hours. The solvent was removed under reduced pressure and ethyl acetate (200ml) was added. The organic phase was washed with saturated brine, dried over anhydrous sodium sulfate and concentrated to an oil.

The crude product was purified by column chromatography on silica gel using ethyl acetate-hexane (1:2) as eluent to give title compounds (0.097g)

EXAMPLE 7

Preparation of 3-(8-chloro-6-fluoro-3-methyl-2H-1,4-benzoxazin-2-one-5-yl) -1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 3-1)

3-[7-Chloro-5-fluoro-2(3H)benzoxazolinon-4-yl]-1-methyl-6-trifluoromethyl-2,4(1H, 3H)-pyrimidinedione (0.50 g) was dissolved in anhydrous toluene (15 ml) and methyl pyruvate (0.15 g) was added. The solution was refluxed with azeotropic removal of water for 2 hours and the solvent was then removed under reduced pressure. The residue was chromatographed on silica gel using hexane-ethyl acetate (3:1) as the eluent to afford the title compound (0.23 g).

EXAMPLE 8

Preparation of 3-(8-chloro-6-fluoro-2-methyl-2H-1,4-benzoxazin-3-one-5-yl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 4-3)

A mixture of 3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-1-methyl-6-trifluromethyl-2,4(1H, 3H)-pyrimidinedione (1.07 g), ethyl bromopropionate (0.61 g) and potassium carbonate (0.414 g) in acetonitrile (30 ml) was stirred at room temperature overnight. The reaction mixture was partitioned between water and ethyl acetate. The organic phase was dried over anhydrous sodium sulfate and evaporated to give an amorphous (0.95 g). The amorphous was purified on a silica gel column, eluted with methylene chloride - ethyl acetate (19 : 1 and 9 : 1) to give the title compound (0.86 g) as white crystals.

EXAMPLE 9

Preparation of 3-(8-chloro-6-fluoro-3,4-dihydro-2H-1,4-benzoxazin-5-yl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 2-1)

A mixture of 3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidinedione (0.4g), 1,2-dibromoethane (0.26g) and potassium carbonate (0.312g) in acetone (30ml) was heated at reflux for 6 hours. The insoluble precipitate was removed through Celite and the filtrate was concentrated to an oil. The oily substance was purified by column chromatography on silica gel using ethyl acetate-hexane (1:2) as eluent to give the title compounds (0.028g).

EXAMPLE 10

Preparation of 3-(4-chloronaphthalen-1-yl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (Compound no. 5-1)

Step1 Preparation of 4-chloronaphthyl isocyanate as an intermediate

To a solution of 4-chloronaphthyl amine(5g) and triethylamine (5.65g) in anhydrous ethyl acetate (100ml) was added dropwise a solution of triphosgene (8.35g) in anhydrous ethyl acetate (100ml) at 0°C. After 15 minutes, the mixture was heated to reflux for1hour under a nitrogen atmosphere. The resulting mixture was allowed to cool to ambient temperature and filtered through Celite to remove the insoluble precipitate. The filtrate was concentrated to give the title compound as black solid.

Step2 To a suspension of sodium hydride (1.23g) in N,N-dimethylformamide (70ml) was added dropwise a solution of ethyl 3-amino-4,4,4-trifluorocrotonate (5.6g) in toluene (50ml) at 0°C under nitrogen atmosphere. After 30 minutes, a solution of 4-chloronaphthyl isocyanate (28mmol) in a mixed solvent of N,N-dimethylformamide (30ml) and toluene (50ml) was added dropwise at same temperature. The resulting solution was stirred for 2 hours at ambient temperature, and then methyl iodide (8g) was added. After 12 hours, the reaction mixture was partitioned with water(200ml) and a mixed solvent of ethyl acetate-hexane (1:1, 300ml). The organic phase was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and obtained solid was washed with hot ethyl acetate to give 3-(4-chloronaphthalen-1-yl)-1-methyl-6-trifluoromethyl-2,4(1H,3H)-pyrimidindione (6.6g) as a brown solid.

EXAMPLE 11

Preparation of 2-(2-*t*-butyl-7-chloro-5-fluorobenzoxazol-4-yl)-5-trifluoromethylpyridazin-3-one
(Compound no. 12-2)

Step 1 Preparation of 2-(4-chloro-6-fluoro-3-methoxy-2-nitrophenyl)-5-trifluoromethylpyridazin-3-one as an intermediate

2-(4-Chloro-2-fluoro-5-methoxyphenyl)-5-trifluoromethylpyridazin-3-one was added to a mixture of conc. sulfuric acid (10ml) and nitric acid (69%, 1ml) with stirring at 0°C. After addition, the cold bath was removed and the resulting mixture was stirred for 0.5 hour at ambient temperature. Addition of the solution to ice-water resulted in yellow precipitate which was collected by filtration. The crude solid was purified by column chromatography on silica gel eluted with ethyl acetate and hexane (1:9) to give the title compound (0.53g). ^{1}H NMR ($CDCl_3$, 300MHz) 4.05 (3H, s), 7.30 (1H, m), 7.53 (1H, d, J=8.7Hz), 8.01 (1H, d, J=2.1Hz) ppm.

Step 2 Preparation of 2-(2-amino-4-chloro-6-fluoro-3-methoxyphenyl)-5-trifluoromethylpyridazin-3-one as an intermediate

A mixture of 2-(4-chloro-6-fluoro-3-methoxy-2-nitrophenyl)-5-trifluoromethylpyridazin-3-one (0.52g) and iron powder (0.4g) in acetic acid (30ml) was stirred overnight at ambient temperature. The reaction solution was poured into water and extracted with ethyl acetate. The organic phase was washed with brine (x3) and dried over anhydrous sodium sulfate. The solvent was removed to give the title compound (0.46g). ^{1}H NMR ($CDCl_3$, 300MHz) 3.88 (3H, s), 4.19 (2H, br s), 6.67 (1H, d, J=9.6Hz), 7.31 (1H, m), 8.10 (1H, d, J=2.2Hz) ppm.

Step 3 Preparation of 2-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-5-trifluoromethylpyridazin-3-one as an intermediate

A mixture of 2-(2-amino-4-chloro-6-fluoro-3-methoxyphenyl)-5-trifluoromethylpyridazin-3-one (0.39g) and borontribromide-methyl sulfide complex (1.8g) in dichloroethane was heated at reflux temperature for 1 hour under nitrogen atmosphere. The mixture was poured into water and extracted with methylene dichloride. The organic phase was dried over anhydrous sodium sulfate and concentrated to give the title compound. ^{1}H

NMR ($CDCl_3$, 300MHz) 4.61 (3H, br s), 6.55 (1H, d, J=9.4Hz), 7.30 (1H, m), 8.05 (1H, d, J=2.2Hz) ppm.

Step 4 Under nitrogen atmosphere 2-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-5-trifluoromethylpyridazin-3-one from step 3 , trimethylacetyl chloride (0.17g), triethylamine (0.14g) and pyridinium *p*-toluenesulfonate in *m*-xylene(30ml) was heated at reflux temperature overnight. The mixture was allowed to cool to ambient temperature and partitioned between ethyl acetate and brine. The organic phase was dried over anhydrous sodium sulfate and concentrated to an oil. The crude product was purified by column chromatography on silica gel eluted with ethyl acetate-hexane (1:8) to afford 2-(2-*t*-butyl-7-chloro-5-fluorobenzoxazol-4-yl)-5-trifluoromethylpyridazin-3-one (0.26g) as a pale yellow solid.

EXAMPLE 12

Preparation of 2-(2-t-butyl-7-chloro-5-fluorobenzoxazol-4-yl)-3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine

(Compound no 11-3)

Step 1 Preparation of 3-chloro-2-(4-chloro-6-fluoro-3-hydroxy-2-nitrophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine as an intermediate

3-Chloro-2-(4-chloro-2-fluoro-5-hydroxyphenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine (1.0g) was slowly added to stirred HNO_3 (69%, 6ml) at 0°C. After 15 minutes, the resulting mixture was poured into ice water and resultant precipitate was separated by filtration to afford the title compound (1.1g). 1H NMR ($CDCl_3$, 300MHz) 1.95(2H, m), 2.10(2H, m), 2.80(2H, t, J=6.3 Hz), 4.17(2H, t, J=6.0 Hz), 6.0(1H, br s), 7.52(1H, d, J=8.2 Hz) ppm.

Step 2 Preparation of 3-chloro-2-(2-amino-4-chloro-6-fluoro-3-hydroxyhenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine

3-Chloro-2-(4-chloro-6-fluoro-3-hydroxy-2-nitrophenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine (1.1g) was dissolved in glacial acetic acid (20ml) and iron powder (0.55g) was added. The suspension was stirred vigorously overnight at ambient temperature. The resulting solution was pertitioned between water and ethyl acetate. The organic phase was washed with saturated brine (x2) , saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed in *vacuo* to afford titled compound as an amorphous solid.1H NMR(DMSO-d_6, 300MHz 1.68(2H, m), 1.82(2H, m), 2.54(2H, t, J=6.1 Hz), 3.93(2H, t, J=5.7 Hz), 4.96(2H, br s), 6.37(1H, d, J=9.5 Hz), 8.82(1H, br s) ppm.

Step 3 3-Chloro-2-(2-amino-4-chloro-6-fluoro-3-hydroxyhenyl)-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine (0.3g), triethylamine (0.12g), pyridinium p-toluenesulfonate (0.14g) and pivaloyl chloride (0.14g) in m-xylene (20ml) was refluxed overnight. Solvent was then evaporated under reduced pressure and the product was subjected to silica gel chromatography eluted with ethyl acetate and hexane (1 : 2). 2-(2-t-butyl-7-chloro-5-fluorobenzoxazol-4-yl)-3-chloro-4,5,6,7-tetrahydropyrazolo[1,5-a]pyridine was obtained (0.34g).

EXAMPLE 13

Preparation of 4-chloro-3-(8-chloro-6-fluoro-2-methyl-2H-1,4-benzoxazine-3-one-5-yl)-5-difluoromethoxy-1-methyl-1H-pyrazole (Compound no. 10-8)

Step 1 Preparation of 4-chloro-3-(4-chloro-6-fluoro-3-hydroxy-2-nitrophenol)-5-difluoromethoxy-1-methyl-1H-pyrazole as an intermediate

4-Chloro-3-(4-chloro-2-fluoro-5-hydroxyphenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole (2.8g) was slowly added to HNO_3 (20ml) at 0°C. The reaction mixture was stirred for 30 minutes at same temperature and poured into ice-water. Yellow precipitate was collected by filtration and washed with water (200ml) to afford the title compound (2.95g).

Step 2 Preparation of 4-chl ro-3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole as an intermediate

A mixture of 4-chloro-3-(4-chloro-6-fluoro-3-hydroxy-2-nitrophenol)-5-difluoromethoxy-1-methyl-1H-pyrazole (2.0g) and iron powder (0.9g) in acetic acid (50ml) was stirred overnight at ambient temperature. The reaction solution was poured into water and extracted with ethyl acetate. The organic phase was washed with brine (x3) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give the title compound (1.9g) as a black oil.

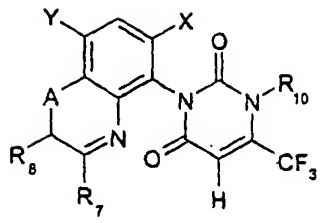
Step 3 A mixture of 4-chloro-3-(2-amino-4-chloro-6-fluoro-3-hydroxyphenyl)-5-difluoromethoxy-1-methyl-1H-pyrazole (0.88g), ethyl 2-bromopropionate (0.70g) and potassiun carbonate (0.711g) in acetonitrile (30ml) was stirred overnight at ambient temperature. The reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed with brine (x3) and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the oily product was subjected to silica gel chromatography eluted with ethyl acetate and hexane (1 : 4) to afford 4-chloro-3-(8-chloro-6-fluoro-2-methyl-2H-1,4-benzoxazine-3-one-5-yl)-5-difluoromethoxy-1-methyl-1H-pyrazole (0.054g).

Using the procedures as described in Schemes 1-17 and Examples 1-12, the compounds of this invention can be readily prepared. Tables 1-17 list structures for few representative compounds of this invention.

The following abbreviations are used in the Tables below.

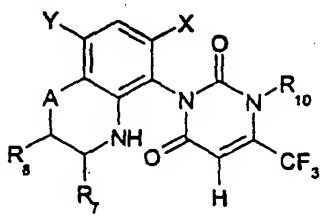
Me:methyl, Et:ethyl, Pr:propyl, Bu:butyl, Ph:phenyl, Ac:acetyl;

Table 1



Compd. No.	X	Y	A	R_7	R_8	R_{10}
1-1	F	Cl	O	H	H	Me
1-2	F	Cl	O	Me	H	Me
1-3	F	Cl	O	Ph	H	Me
1-4	F	Cl	O	Me	H	NH2
1-5	H	Cl	O	Me	Me	Me
1-6	F	Cl	O	Me	Me	Me
1-7	F	Cl	NH	Me	Me	Me
1-8	F	Cl	S	Me	Me	Me
1-9	F	CN	O	Me	H	Me
1-10	F	Cl	O	CO_2Me	H	Me
1-11	F	Cl	O		H	Me

Table 2



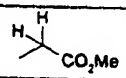
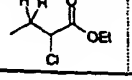
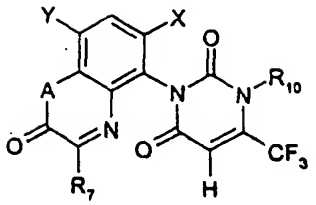
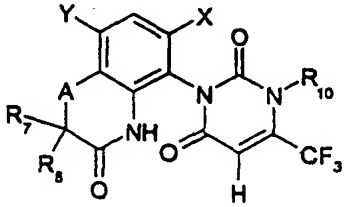
Compd. No.	X	Y	A	R_7	R_8	R_{10}
2-1	F	Cl	O	H	H	Me
2-2	F	Cl	S	H	H	Me
2-3	F	Cl	O	H	H	NH2
2-4	F	Cl	NH	H	H	Me
2-5	F	Cl	O	Me	H	Me
2-6	F	Cl	O	Me	Me	Me
2-7	F	CN	O	H	H	Me
2-8	F	Cl	O	H		Me
2-9	F	Cl	O	H		Me

Table 3



Compd. No.	X	Y	A	R_7	R_{10}
3-1	F	Cl	O	Me	Me
3-2	F	Cl	NH	Me	Me
3-3	F	Cl	S	Me	Me
3-4	F	Cl	O	Ph	Me
3-5	F	Cl	O	CO_2Et	Me
3-6	F	Cl	O	Me	NH_2

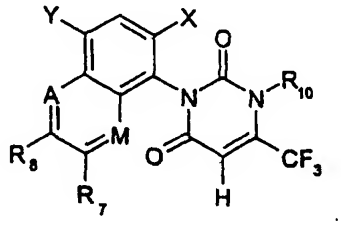
Table 4



Compd. No.	X	Y	A	R_7	R_8	R_{10}
4-1	F	Cl	O	H	H	Me
4-2	F	Cl	O	H	H	NH_2
4-3	F	Cl	O	Me	H	Me
4-4	F	Cl	S	H	H	Me
4-5	F	Cl	NH	H	H	Me
4-6	F	Cl	CH_2	H	H	Me
4-7	F	Cl	O	CO_2Me	H	Me
4-8	F	Cl	O		H	Me
4-9	F	Cl	O	Ph	H	Me
4-10	F	Cl	O	Me	M	Me
4-11	F	Cl	O	-CH$_2$CH(Cl)CO$_2$Et	H	Me
4-12	F	Cl	O	-CH$_2$CH(Cl)CO$_2$Et	Me	Me

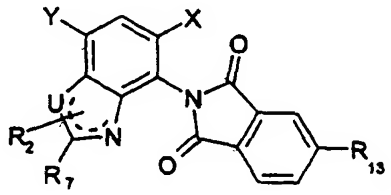
4-13	F	Cl	O	Cl	H	Me
4-14	Cl	Cl	O	Me	Me	Me

Table 5



Compd. No.	X	Y	A	M	R_7	R_8	R_{10}
5-1	H	Cl	CH	CH	H	H	Me
5-2	F	Cl	CH	CH	H	H	Me
5-3	F	Cl	CH	CH	Me	H	Me
5-4	F	Cl	CH	N	H	H	Me
5-5	F	Cl	N	CH	H	H	Me
5-6	F	Cl	CH	CH	Me	Me	Me
5-7	F	Cl	N	N	H	H	Me
5-8	F	Cl	CH	CH	H	CO_2Me	Me
5-9	F	Cl	CH	CH		H	Me
5-10	F	Cl	CNO_2	CH	H	H	Me
5-11	F	Cl	CH	CH	H	H	NH_2

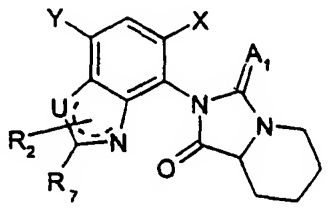
Table 6



Compd. No.	X	Y	U	R_2	R_7	R_{13}
6-1	F	Cl	O	-	Me	H
6-2	F	Cl	O	-	t-Bu	H
6-3	F	Cl	S	-	t-Bu	H
6-4	F	Cl	O	-	t-Bu	F

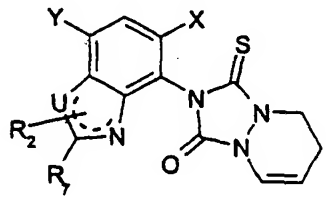
6-5	F	Cl	N	H	t-Bu	H

Table 7



Compd. No.	X	Y	U	R_2	R_7	A_1
7-1	F	Cl	N	H	Me	S
7-2	F	Cl	N	H	Et	S
7-3	F	Cl	N	H	t-Bu	S
7-4	F	Cl	O	-	Me	S
7-5 rotamer 2	F	Cl	O	-	Et	S
7-6 rotamer 1	F	Cl	O	-	Et	S
7-7	F	Cl	O	-	t-Bu	S
7-8	F	Cl	O	-	Me	O
7-9	F	Cl	O	-	Et	O
7-10	F	Cl	N	H	t-Bu	O
7-11	F	Cl	N	H	t-Bu	O

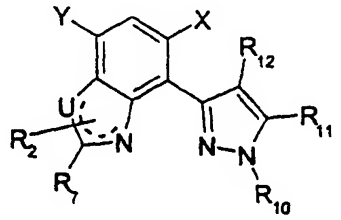
Table 8



Compd. No.	X	Y	U	R_2	R_7
8-1	F	Cl	O	-	Et
8-2	F	Cl	O	-	t-Bu
8-3	F	Cl	S	-	t-Bu
8-4	F	Cl	N	H	t-Bu

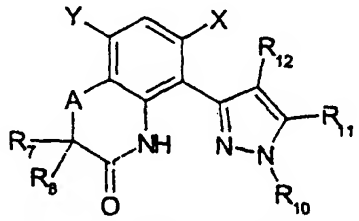
8-5	F	Cl	N	Me	t-Bu

Table 9



Compd. No.	X	Y	U	R_2	R_7	R_{10}	R_{11}	R_{12}
9-1	F	Cl	N	H	Et	Me	CF_3	Cl
9-2	Cl	Cl	N	H	Et	Me	CF_3	Cl
9-3	F	Cl	N	H	t-Bu	Me	CF_3	Cl
9-4	F	Cl	N	H	t-Bu	Me	CF_3	Br
9-5	H	Cl	N	H	t-Bu	Me	CF_3	Cl
9-6	Cl	Cl	N	H	t-Bu	Me	CF_3	Cl
9-7	F	Cl	N	H	t-Bu	Me	$OCHF_2$	Cl
9-8	F	Cl	N	Me	t-Bu	Me	CF_3	Cl
9-10	F	Cl	N	H	CH_2CO_2Me	Me	CF_3	

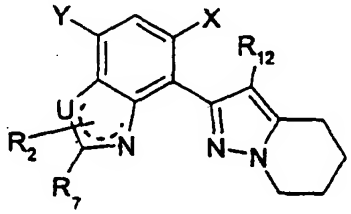
Table 10



Compd. No.	X	Y	A	R_7	R_8	R_{10}	R_{11}	R_{12}
10-1	F	Cl	O	H	H	Me	CF_3	Cl
10-2	F	Cl	O	Me	H	Me	CF_3	Cl
10-3	F	Cl	O	Me	Me	Me	CF_3	Cl
10-4	Cl	Cl	O	H	H	Me	CF_3	Cl
10-5	F	Br	O	Me	Me	Me	CF_3	Cl
10-6	F	Cl	O	Me	Me	Me	CF_3	Br
10-7	H	Cl	O	Me	Me	Me	CF_3	Cl
10-8	F	Cl	O	Me	H	Me	$OCHF_2$	Cl
10-9	F	Cl	O	Me	Me	Me	$OCHF_2$	Cl
10-10	F	Cl	O	Me	Me	Me	$OCHF_2$	Br

10-11	H	Cl	O	Me	H	Me	$OCHF_2$	Cl
10-12	F	F	O	Me	Me	Me	$OCHF_2$	Cl
10-13	F	Cl	NH	H	H	Me	$OCHF_2$	Cl
10-14	F	Cl	O	H	H	Me	$OCHF_2$	Cl
10-15	F	Cl	S	H	H	Me	CF_3	Cl
10-16	F	Cl	S	Me	H	Me	$OCHF_2$	Cl
10-17	F	Cl	O	Me	Me	Me	$OCHF_2$	CN

Table 11



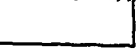
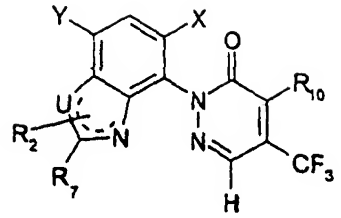
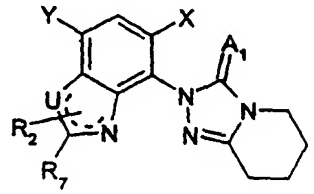
Compd. No.	X	Y	U	R_2	R_7	R_{12}
11-1	H	Cl	O	-	t-Bu	Cl
11-2	Cl	Cl	O	-	t-Bu	Cl
11-3	F	Cl	O	-	t-Bu	Cl
11-4	F	Cl	N	H	Me	Cl
11-5	F	Cl	O	-	t-Bu	Br
11-6	F	Cl	O	-	t-Bu	CN
11-7	F	Cl	O	-	Me	Cl
11-8	H	Cl	S	-	t-Bu	Cl
11-9	F	Cl	O	-	t-Bu	

Table 12



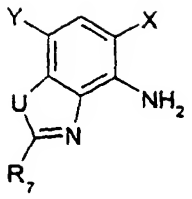
Compd. No.	X	Y	U	R_2	R_7	R_{10}
12-1	F	Cl	O	-	Me	H
12-2	F	Cl	O	-	t-Bu	H
12-3	F	Cl	O	-	t-Bu	Me
12-4	F	Cl	S	-	t-Bu	Me
12-5	F	Cl	N	H	t-Bu	Me
12-6	F	Cl	N	Me	t-Bu	Me

Table 13



Compd. No.	X	Y	U	R_2	R_7	A_1
13-1	H	Cl	O	-	Me	O
13-2	H	Cl	O	-	t-Bu	O
13-3	F	Cl	O	-	t-Bu	O
13-4	Cl	Cl	O	-	t-Bu	O
13-6	F	F	O	-	t-Bu	O
13-7	F	Cl	N	H	t-Bu	O
13-8	F	Cl	O	-	t-Bu	S
13-9	F	Cl	S	-	t-Bu	O
13-10	F	Cl	S	-	Me	O

Table 14



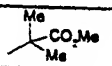
Compd. No.	X	Y	U	R_7
14-1	F	Cl	O	H
14-2	F	Cl	O	Me
14-3	F	Cl	O	Et
14-4	F	Cl	O	t-Bu
14-5	F	Cl	O	
14-6	F	Cl	O	
14-7	F	Cl	O	
14-8	F	Cl	O	
14-9	H	Cl	O	t-Bu
14-10	Cl	Cl	O	t-Bu
14-11	F	Cl	S	Me
14-12	F	CN	O	Me
14-13	F	CN	O	t-Bu
14-14	F	CF_3	O	t-Bu
14-15	F	Cl	NH	t-Bu
14-16	F	$OCHF_2$	O	Et
14-17	F	NO2	O	t-Bu
14-18	F	Br	O	t-Bu
14-19	F	F	O	t-Bu

Table 15 lists some of the characterization data for a few representative compounds of this invention.

Table 15

Compd. No.	^{1}H-NMR(300MHz, ppm)
1-3	3.57(3H, s), 5.15(1H, d, J=15.3Hz), 5.20(1H, d, J=15.3Hz), 6.40(1H, s), 7.15(1H, d, J=9.0Hz), 7.4-7.8(5H, m).
2-1	3.57(3H, d, J=1.1Hz), 3.71(2H, dd, J=5.4, 4.2Hz), 4.28(1H, br s), 4.38(2H, dd, J=5.4, 4.2Hz),6.37(1H, s), 6.65(1H, d, J=9.3Hz).
3-1	2.55(3H, s), 3.58(3H, br d, J=1.1 Hz), 6.39(1H, s), 7.49(1H, d, J=8.7 Hz).
4-1	3.45 (3H, s), 4.75 (2H, s), 6.59 (1H, s), 7.27 (1H, d, J=9.4 Hz), 11.13 (1H, s).
4-2	4.70 (2H, s), 5.55 (2H, s), 6.28 (1H, s), 7.14 (1H, d, J=9.3 Hz), 11.21 (1H, s).
4-3	1.45(1.5H, d, J=6.8 Hz), 1.47(1.5H, d, J=6.8 Hz), 3.44 (3H, s), 4.84 (0.5H, q, J=6.8 Hz), 4.86 (0.5H, q, J=6.8Hz), 6.60 (1H, s), 7.29 (1H, d, J=9.4 Hz), 11.10(0.5H, s), 11.12 (0.5H, s).
4-10	1.41(3H, s), 1.45(3H, s), 3.43(3H, s), 6.65(1H, s), 7.36(1H, d, J=9.5 Hz).
5-1	3.59(3H, br d J=1.3Hz), 6.45(1H, s), 7.31(1H, d, J=7.9Hz), 7.5-7.7(4H, m), 8.36(1H, dd, J=7.6, 0.5Hz).
6-2	1.47(9H, s), 7.60(1H, d, J=10.2 Hz), 7.90-8.10(4H, m).
7-5	1.43(3H, t, J=7.6Hz), 1.63(3H, m), 1.9(1H, m), 2.1(1H, m), 2.4(1H, m), 2.99(2H, q, J=7.6Hz), 4.17(1H, m), 4.90(1H, m), 7.25(1H, d, J=9.6Hz).
7-6	1.43(3H, t, J=7.6Hz), 1.7(3H, m), 1.9(1H, m), 2.1(1H, m), 2.37(1H, m), 2.97(2H, q, J=7.6Hz), 3.13(1H, m), 4.13(1H, m), 4.89(1H, m), 7.24(1H, d, J=9.7Hz).
7-9	1.43(3H, t, J=7.6), 1.57(3H, m), 1.79(1H, m), 2.08(1H, m), 2.34(1H, m), 2.99(2H, 2q), 4.05(1H, m), 4.26(1H, m), 7.25(1H, 2d).
8-1	1.44(3H, t, J=7.4Hz), 2.60(2H, m), 3.02(2H, q, J=7.6Hz), 4.32(2H, m), 5.40(1H, m), 6.89(1H, d, J=8.2Hz), 7.30(1H, d, J=9.8Hz).

10-8	1.62(3H, d, J=6.8 Hz), 3.87(3H, s), 4.70(1H, q, J=6.8 Hz), 6.74(1H, t, J=72.0 Hz), 6.92(1H, d, J=9.3 Hz), 8.91(1H, br s).
10-9	1.56(6H, s), 3.88(3H, s), 6.74(1H, t, J=72.0 Hz), 6.92(1H, d, J=9.4 Hz), 8.82(1H, Br s).
11-3	1.49(9H, s), 1.94(2H, m), 2.08(2H, m), 2.79(2H, t, J=6.3 Hz), 4.22(2H, t, J=5.9 Hz), 7.18(1H, d, J=10.0 Hz).
14-3	1.45 (3H, t, J=7.6Hz), 2.96 (2H, q, J=7.5Hz), 4.28 (2H, br s), 7.01(1H, d, J=11.2Hz).
14-18	1.48 (9H, s), 4.25 (2H, br s), 7.12 (1H, d, J=11.0Hz).

HERBICIDAL ACTIVITY

The compounds of the present invention exhibit excellent herbicidal effects when used as an active ingredient of a herbicide. The herbicide can be used for a wide range of applications, for example on crop lands such as paddy fields, upland farms, orchards, vinyards and mulberry fields, and non-crop lands such as forests, turf, rights of way, roadsides, railways, farm roads, playgrounds, and factory sites. The application method may be suitably selected for soil treatment application and foliar application.

The compounds of the present invention are capable of controlling noxious weeds including grass (gramineae) such as barnyardgrass (*Echinochloa crus-galli*), large crabgrass (*Digitaria sanguinalis*), green foxtail (*Setaria viridis*), goosegrass (*Eleusine indica* L.), wild oat (*Avena fatua* L.), Johnsongrass (*Sorghum halepense*), quackgrass (*Agropyron repens*), alexandergrass (*Brachiaria plantaginea*), paragrass (*Panicum purpurascen*), sprangletop (*Leptochloa chinensis*) and red sprangletop (*Leptochloa panicea*); sedges (or Cyperaceae) such as rice flatsedge (*Cyperus iria* L.), purple nutsedge (*Cyperus rotundus* L.), Japanese bulrush (*Scirpus Juncoides*), flatsedge (*Cyperus serotinus*), small-flower umbrellaplant (*Cyperus difformis*), slender spikerush (*Eleocharis acicularis*), and water chestnut (*Eleocharis kuroguwai*); alismataceae such as Japanese ribbon wapato (*Sagittaria pygmaea*), arrow-head (*Sagittaria trifolia*) and narrowleaf waterplantain (*Alisma canaliculatum*); pontederiaceae such as monochoria (*Monochoria vaginalis*) and monochoria species (*Monochoria korsakowii*); scrophulariaceae such as false pimpernel (*Lindernia pyxidaria*) and abunome (*Dopatrium Junceum*); lythraceae such as toothcup (*Rotala indica*) and red stem (*Ammannia multiflora*); and broadleaves such as redroot pigweed (*Amaranthus retroflexus*), velvetleaf (*Abutilon theophrasti*), morningglory (*Ipomoea hederacea*), lambsquarters (*Chenopodium album*), prickly sida (*Sida spinosa* L.), common purslane (*Portulaca oleracea* L.), slender amaranth (*Amaranthus viridis* L.), sicklepod (*Cassia obtusifolia*), black nightshade (*Solanum nigrum* L.), pale smartweed (*Polygonum lapathifolium* L.), common chickweed (*Stellaria media* L.), common cocklebur (*Xanthium strumarium* L.), flexuous bittercress (*Cardamine flexuosa* WITH.), henbit (*Lamium amplexicaule* L.) and threeseeded copperleaf (*Acalypha australis* L.). Accordingly, it is useful for controlling noxious weeds non-selectively or selectively in the cultivation of a crop

plant such as corn (*Zea mays* L.), soybean (*Glycine max* Merr.), cotton (*Gossypium* spp.), wheat (*Triticum* spp.), rice (*Oryza sativa* L.), barley (*Hordeum vulgare* L.), oat (*Avena sativa* L.), sorghum (*Sorghum bicolor* Moench), canola (*Brassica napus* L.), sunflower (*Helianthus annuus* L.), sugar beet (*Beta vulgaris* L.), sugar cane (*Saccharum officinarum* L.), Japanese lawngrass (*Zoysia Japonica stend*), peanut (*Arachis hypogaea* L.) or flax (*Linum usitatissimum* L.).

For use as herbicides, the active ingredients of this invention are formulated into herbicidal compositions by mixing herbicidally active amounts with inert ingredients known to the art to facilitate either the suspension, dissolution or emulsification of the active ingredient for the desired use. The type of formulation prepared recognizes the facts that formulation, crop and use pattern all can influence the activity and utility of the active ingredient in a particular use. Thus for agricultural use the present herbicidal compounds may be formulated as water dispersible granules, granules for direct application to soils, water soluble concentrates, wettable powders, dusts, solutions, emulsifiable concentrates (EC), microemulsion, suspoemulsion, invert emulsion or other types of formulations, depending on the desired weed targets, crops and application methods.

These herbicidal formulations may be applied to the target area (where suppression of unwanted vegetation is the objective) as dusts, granules or water or solvent diluted sprays. These formulation may contain as little as 0.1% to as much as 97% active ingredient by weight.

Dusts are admixtures of the active ingredient with finely ground materials such as clays (some examples include kaolin and montmorillonite clays), talc, granite dust or other organic or inorganic solids which act as dispersants and carriers for the active ingredient; these finely ground materials have an average particle size of less than 50 microns. A typical dust formulation will contain 1 % active ingredient and 99% carrier.

Wettable powders are composed of finely ground particles which disperse rapidly in water or other spray carriers. Typical carriers include kaolin clays, Fullers earth, silicas and other absorbent, wettable inorganic materials. Wettable powders can be prepared to contain from 1 to 90% active ingredient, depending on the desired use pattern and the absorbability of

the carrier. Wettable powders typically contain wetting or dispersing agents to assist dispersion in water or other carriers.

Water dispersible granules are granulated solids that freely disperse when mixed in water. This formulation typically consists of the active ingredient (0.1% to 95% active ingredient), a wetting agent (1-15% by weight), a dispersing agent (1 to 15% by weight) and an inert carrier (1-95% by weight). Water dispersible granules can be formed by mixing the ingredients intimately then adding a small amount of water on a rotating disc (said mechanism is commercially available) and collecting the agglomerated granules. Alternatively, the mixture of ingredients may be mixed with an optimal amount of liquid (water or other liquid) and passed through an extruder (said mechanism is commercially available) equipped with passages which allow for the formation of small extruded granules. Alternatively, the mixture of ingredients can be granulated using a high speed mixer (said mechanism is commercially available) by adding a small amount of liquid and mixing at high speeds to affect agglomeration. Alternatively, the mixture of ingredients can be dispersed in water and dried by spraying the dispersion through a heated nozzle in a process known as spray drying (spray drying equipment is commercially available). After granulation the moisture content of granules is adjusted to an optimal level (generally less than 5%) and the product is sized to the desired mesh size.

Granules are granulated solids that do not disperse readily in water, but instead maintain their physical structure when applied to the soil using a dry granule applicator. These granulated solids may be made of clay, vegetable material such as corn cob grits, agglomerated silicas or other agglomerated organic or inorganic materials or compounds such as calcium sulfate. The formulation typically consists of the active ingredient (1 to 20%) dispersed on or absorbed into the granule. The granule may be produced by intimately mixing the active ingredient with the granules with or without a sticking agent to facilitate adhesion of the active ingredient to the granule surface, or by dissolving the active ingredient in a solvent, spraying the dissolved active ingredient and solvent onto the granule then drying to remove the solvent. Granular formulations are useful where in-furrow or banded application is desired.

Emulsifiable concentrates (EC) are homogeneous liquids composed of a solvent or mixture of solvents such as xylenes, heavy aromatic naphthas, isophorone or other proprietary commercial compositions derived from petroleum distillates, the active ingredient and an emulsifying agent or agents. For herbicidal use, the EC is added to water (or other spray carrier) and applied as a spray to the target area. The composition of an EC formulation can contain 0.1% to 95% active ingredient, 5 to 95% solvent or solvent mixture and 1 to 20% emulsifying agent or mixture of emulsifying agents.

Suspension concentrate (also known as flowable) formulations are liquid formulations consisting of a finely ground suspension of the active ingredient in a carrier, typically water or a non-aqueous carrier such as an oil. Suspension concentrates typically contain the active ingredient (5 to 50% by weight), carrier, wetting agent, dispersing agent, anti-freeze, viscosity modifiers and pH modifiers. For application, suspension concentrates are typically diluted with water and sprayed on the target area.

Solution concentrates are solutions of the active ingredient (1 to 70%) in solvents which have sufficient solvency to dissolve the desired amount of active ingredient. Because they are simple solutions without other inert ingredients such as wetting agents, additional additives are usually added to the spray tank mix before spraying to facilitate proper application.

Microemulsions are solutions consisting of the active ingredient (1 to 30%) dissolved in a surfactant or emulsifier, with additional solvents. Microemulsions are particularly useful when a low odor formulation is required such as in residential turfgrass applications.

Suspoemulsions are combinations of two active ingredients. One active ingredient is made as a suspension concentrate (1-50% active ingredient) and the second active is made as a emulsifiable concentrate (0.1 to 20%). A reason for making this kind of formulation is the inability to make an EC formulation of the first ingredient due to poor solubility in organic solvents. The suspoemulsion formulation allows for the combination of the two active ingredients to be packaged in one container, thereby minimizing packaging waste and giving greater convenience to the product user.

The herbicidal compounds of this invention may be formulated or applied with insecticides, fungicides, acaricides, nematicides, fertilizers, plant growth regulators or other agricultural chemicals. Certain tank mix additives, such as spreader stickers, penetration aids, wetting agents, surfactants, emulsifiers, humectants and UV protectants may be added in amounts of 0.01% to 5% to enhance the biological activity, stability, wetting, spreading on foliage or uptake of the active ingredients on the target area or to improve the suspensibility, dispersion, redispersion, emulsifiability, UV stability or other physical or physico-chemical property of the active ingredient in the spray tank, spray system or target area.

The compositions of the present invention may be used in admixture with or in combination with other agricultural chemicals, fertilizers, adjuvants, surfactants, emulsifiers, oils, polymers or phytotoxicity-reducing agents such as herbicide safeners. In such a case, they may exhibit even better effects or activities. As other agricultural chemicals, herbicides, fungicides, antibiotics, plant hormones, plant growth regulators, insecticides, or acaricides may, for example, be mentioned. Especially with herbicidal compositions having the compounds of the present invention used in admixture with or in combination with one or more active ingredients of other herbicides, it is possible to improve the herbicidal activities, the range of application time(s) and the range of applicable weed types. Further, the compounds of the present invention and an active ingredient of another herbicide may be separately formulated so they may be mixed for use at the time of application, or both may be formulated together. The present invention covers such herbicidal compositions.

The blend ratio of the compounds of the present invention with the active ingredient of other herbicides can not generally be defined, since it varies depending on the time and method of application, weather conditions, soil type and type of formulation. However one active ingredient of other herbicide may be incorporated usually in an amount of 0.01 to 100 parts by weight , per one part by weight of the compounds of the present invention. Further, the total dose of all of the active ingredients is usually from 1 to 10000 g/ha, preferably from 5 to 500 g/ha. The present invention covers such herbicidal compositions.

As the active ingredients of other herbicides, the following (common name) may be mentioned. Herbicidal compositions having the compounds of the present invention used in

combination with other herbicides, may occasionally exhibit a synergistic effect.

1. Those that are believed to exhibit herbicidal effects by disturbing auxin activities of plants, including a phenoxy acetic acid type such as 2,4-D, 2,4-DB, 2,4-DP, MCPA, MCPP, MCPB or naproanilide (including the free acids, esters or salts thereof), an aromatic carboxylic type such as 2,3,6 TBA, dicamba, dichlobenil, a pyridine type such as picloram (including free acids and salts thereof), triclopyr or clopyralid and others such as naptalam, benazolin, quinclorac, quinmerac or diflufenzopyr (BAS 654H).

2. Those that are believed to exhibit herbicidal effects by inhibiting photosynthesis of plants including a urea type such as diuron, linuron, isoproturon, chlorotoluron, metobenzuron, tebuthiuron or fluometuron, a triazine type such as simazine , atrazine, cyanazine, terbuthylazine, atraton, hexazinone, metribuzin, simetryn, ametryn, prometryn, dimethametryn or triaziflam, a uracil type such as bromacil, terbacil or lenacil, an anilide type such as propanil or cypromid, a carbamate type such as desmedipham or phenmedipham, a hydroxybenzonitrile type such as bromoxynil or ioxynil, and others such as pyridate, bentazon and methazole.

3. A quaternary ammonium salt type such as paraquat, diquat or difenzoquat, which is believed to form active oxygen in the plant and thus to exhibit quick herbicidal effects.

4. Those which are believed to exhibit herbicidal effects by inhibiting chlorophyll biosynthesis in plants and abnormally accumulating a photsensitizing peroxide substance in the plant body, including a diphenyl ether type such as nitrofen, lactofen, acifluorfen-sodium, oxyfluorfen, fomesafen, bifenox, or chlomethoxyfen, a cyclic imide type such as chlorphthalim, flumioxazin, cinidon-ethyl, or flumiclorac-pentyl, and others such as oxadiazon, sulfentrazone, thidiazimin, azafenidin, carfentrazone, isopropazole, fluthiacet-methyl, pentoxazone, pyraflufen-ethyl and oxadiargyl.

5. Those which are believed to exhibit herbicidal effects characterized by whitening activities by inhibiting chromogenesis of plants such as carotenoids including a pyridazinone type such as norflurazon, chloridazon or metflurazon, a pyrazol type such as pyrazolate, pyrazoxyfen or benzofenap, and others such as fluridone, fluramone, diflufencam, methoxyphenone, clomazone, amitrole, sulcotrione, mesotrione, isoxaflutole and isoxachlortole.

6. Those which exhibit herbicidal effects specifically to gramineous plants including an aryloxyphenoxypropionic acid type (either as a mixture of isomers or as a resolved isomer)

such as diclofop-methyl, pyrofenop-sodium, fluazifop butyl or fluazifop-p-butyl, haloxyfop-methyl, quizalofop p-ethyl, quizalafop p-tefuryl, fenoxaprop ethyl or fenoxaprop-p-ethyl, flamprop-M-methyl or flamprop-m-isopropyl or cyhalofop-butyl and a cyclohexanedione type such as alloxydim-sodium, sethoxydim, clethodim, tepraloxydim or tralkoxydim.

7. Those which are believed to exhibit herbicidal effects by inhibiting amino acid biosynthesis of plants, including a sulfonylurea type such as chlorimuron-ethyl, nicosulfuron, metsulfuron-methyl, triasulfuron, primisulfuron, tribenuron-methyl, chlorosulfuron, bensulfuron-methyl, sulfometuron-methyl, prosulfuron, halosulfuron or halosulfuron-methyl, thifensulfuron-methyl, rimsulfuron, azimsulfuron, flazasulfuron, imazosulfuron, cyclosulfamuron, flupyrsulfuron, iodosulfuron, ethoxysulfuron, flucarbazone, sulfosulfuron, oxasulfuron a triazolopyrimidinesulfonamide type such as flumetsulam, metosulam, chloransulam or chloransulam-methyl, an imidazolinone type such as imazapyr, imazethapyr, imazaquin, imazamox, imazameth, imazamethabenz methyl, a pyrimidinesalicylic acid type such as pyrthiobac-sodium, bispyribac-sodium, pyriminobac-methyl or pyribenzoxim (LGC-40863), and others such as glyphosate, glyphosate-ammonium, glyphosate-isopropylamine or sulfosate.

8. Those which are believed to exhibit herbicidal effects by interfering with the normal metabolism of inorganic nitrogen assimilation such as glufosinate, glufosinate-ammonium, phosphinothricin or bialophos.

9. Those which are believed to exhibit herbicidal effects by inhibiting cell division of plant cells, including a dinitroaniline type such as trifluralin, oryzalin, nitralin, pendamethalin, ethafluralin, benefin and prodiamine, an amide type such as bensulide, napronamide, and pronamide, a carbamate type such as propham, chlorpropham, barban, and asulam, an organophosphorous type such as amiprofos-methyl or butamifos and others such as DCPA and dithiopyr.

10. Those which are believed to exhibit herbicidal effects by inhibiting protein synthesis of plant cells, including a chloroacetanilide type such as alachlor, metolachor (including combinations with safeners such as benoxacor, or resolved isomeric mixtures of metolachlor including safeners such as benoxacor) propachlor, acetochlor (including combinations with herbicide safeners such as dichlormid or MON 4660 or resolved isomeric mixtures of acetochlor containing safeners such as dichlormid or MON 4660), propisochlor or dimethenamid or an oxyacetamide type such as flufenacet.

11. Those in which the mode of action causing the herbicidal effects are not well understood including the dithiocarbamates such as thiobencarb, EPTC, diallate, triallate, molinate, pebulate, cycloate, butylate, vernolate or prosulfocarb and miscellaneous herbicides such as MSMA, DSMA, endothall, ethofumesate, sodium chlorate, pelargonic acid and fosamine.

A few formulation examples of the present invention are given as follows.

Formulation example 1. ***Emulsifiable Concentrate***

Ingredient Trade Name	**Chemical Name**	**Supplier**	**Function**	**% wt./wt.**
Compound 4-3			Active Ingredient	5.0
Toximul H-A	Calcium sulfonate and nonionic surfactant blend	Stepan Co.	Emulsifier	2.5
Toximul D-A	Calcium sulfonate and nonionic surfactant blend	Stepan Co.	Emulsifier	7.5
Aromatic 200	Aromatic hydrocarbon	Exxon Chemical Co.	Solvent	QS to 100%

Formulation example 2. ***Suspension Concentrate***

Ingredient Trade Name	**Chemical Name**	**Supplier**	**Function**	**% wt./wt.**
Compound 2-1			Active Ingredient	10.00
Proylene gylcol			Anti-freeze	5.00
Antifoam 1530	Silicone defoamer	Dow Corning	Anti-foam	0.50
Rhodopol 23	Xanthan gum	Rhone-Poulenc	Suspending Aid	0.25
Morwet D-425	Napthalene formaldehyde condensate	Witco Corp.	Dispersant	3.00
Igepal CA-720	Octylphenol ethoxylate	Rhone-Poulenc	Wetting agent	3.00
Proxel GXL	1,2 benziso-thiazolin-3-one	ICI Americas	Preservative	0.25
Water			Diluent	68.00

Formulation example 3. *Wettable Powder*

Ingredient Trade Name	Chemical Name	Supplier	Function	% wt./wt.
Compound 8-1			Active Ingredient	50.00
Geropon T-77	Sodium -N-methyl-N-oleoyl taurate	Rhone-Poulenc	Wetting agent	3.00
Lomar PW	Napthalene Sulfonate	Henkel Corp.	Dispersant	5.00
Kaolin clay	Kaolin clay	J. M. Huber	Filler	42.00

Formulation example 4. *Water Dispersible Granule*

Ingredient Trade Name	Chemical Name	Supplier	Function	% wt./wt.
Compound 10-8			Active Ingredient	50.00
Morwet EFW		Witco Corp.	Wetting agent	2.00
Morwet D-425	Napthalene formaldehyde condensate	Witco Corp.	Dispersant	10.00
ASP 400	Kaolin Clay	Engelhard Corp.	Filler	38.00

Test Example

A standard greenhouse herbicide activity screening system was used to evaluate the herbicidal efficacy and crop safety of these test compounds. Seven broadleaf weed species including redroot pigweed (*Amaranthus retroflexus*, AMARE), velvetleaf (*Abutilon theophrasti*, ABUTH), sicklepod (*Cassia obtusifolia*, CASOB), ivyleaf morningglory (*Ipomoea hederacea*, IPOHE), lambsquarters (*Chenopodium album*, CHEAL), common ragweed (*Ambrosia artemisiifolia* L., AMBEL), and cocklebur (*Xanthium strumarium*, XANST) were used as test species. Four grass weed species including green foxtail (*Setaria viridis*, SETVI), barnyardgrass (*Echinochloa crus-galli*, ECHCG), johnsongrass (*Sorghum halepense*, SORHA), and large crabgrass (*Digitaria sanguinalis*, DIGSA) were also used. In addition, three crop species, field corn (*Zea mays* L., var. Dekalb 527, CORN), soybean (*Glycine max* L., var. Pella 86, SOY), and upland rice (*Oryza sp.*, var.Tebonnet, RICE) were included.

Pre-emerge test

All plants were grown in 10 cm square plastic pots which were filled with a sandy loam soil mix. For pre-emerge tests, seeds were planted one day prior to application of the test compounds. For post-emerge tests, seeds were planted 8-21 days prior to the test to allow emergence and good foliage development prior to application of the test substances. At the time of the post-emerge application, plants of all species were usually at the 2-3 leaf stage of development.

All test compounds were dissolved in acetone and applied to the test units in a volume of 187 l/ha. Test materials were applied at rates ranging from 15 g ai/ha to 1000 g ai/ha using a track sprayer equipped with a TJ8001E even flow flat fan spray nozzle. Plants were arranged on a shelf so that the top of the canopy (post-emerge) or top of the soil surface (pre-emerge) was 40-45 cm below the nozzle. Pressurized air was used to force the test solution through the nozzle as it was mechanically advanced over the top of all test plants/pots. This application simulates a typical commercial field herbicide application.

Post-emerge test

In the post-emerge test, a commercial non-ionic surfactant was also included (0.25% v/v) to enhance wetting of the leaf surfaces of target plants. Immediately after application, test units of the pre-emerge applications were watered at the soil surface to incorporate the test materials.

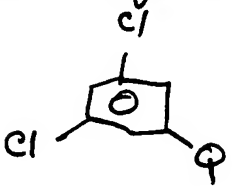
At 14 days after application of the test materials, phytotoxicity ratings were recorded. A rating scale of 0-100 was used as previously described in *Research Methods in Weed Science*, 2nd edition, B. Truelove, Ed., Southern Weed Science Society, Auburn University, Auburn, Alabama, 1977. Briefly, "0" corresponds to no damage and "100" corresponds to complete death of all plants in the test unit. This scale was used both to determine efficacy against weed species and damage to crop species. Herbicide activity data for various compounds of this invention, which are shown by compound No. in Tables 1-14, are shown in Tables 16 and 17. The data demonstrate significant differences between compounds for both efficacy against weeds and selectivity for crop species. For selected compounds,

4-2	250	100	100	90	100	100	----	40	60	----	20	100	90	90
4-3	250	100	100	95	100	100	----	50	80	90	70	100	100	80
5-1	500	100	100	60	60	100	---	100	70	---	60	0	0	0
7-5	250	100	100	100	100	100	----	60	0	0	10	80	20	10
7-6	250	30	90	30	70	60	----	10	0	----	0	50	30	10
8-1	250	100	100	100	100	99	----	100	90	99	70	100	80	80
10-8	250	100	100	100	100	100	95	100	100	55	65	100	25	90
12-1	250	70	95	10	40	0	20	0	50	0	0	50	0	10

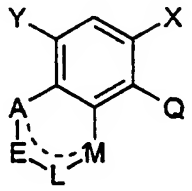
WHAT IS CLAIMED IS :

1. A compound of the formula or its salt represented by the formula (Ia) or (Ib).

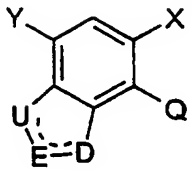
Would require :



Cer - compounds



(Ia)



(Ib)

in which

X, Y are independent of each other and are represented by hydrogen, halogen, cyano, nitro, (C_{1-4})alkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkyl or (C_{1-4})haloalkoxy;

A is oxygen, nitrogen, NR_1, CR_3, CR_3R_4, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_1)$;

D is nitrogen or NR_2;

M is CR_5, CR_5R_6, nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

When A is oxygen, M is nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

E and L are independent of each other and may be selected from CR_7, CR_8, CR_7R_8, oxygen, nitrogen, NR_7, $S(O)_{n*}$, C(=O), C(=S), $C(=NR_7)$ or CNR_7R_8;

U is CR_9, oxygen, nitrogen, NR_2, $S(O)_{n*}$, C(=O), C(=S) or $C(=NR_2)$;

When U is CR_9, E is nitrogen;

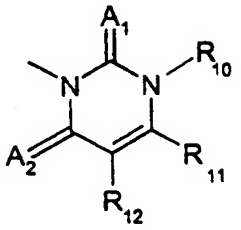
R_1 and R_2 are independent of each other and may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{2-6})alkenyl, (C_{2-6})alkynyl, (C_{1-6})alkylcarbonyl, (C_{-6})cycloalkylcarbonyl, (C_{1-6})haloalkylcarbonyl, (C_{1-6})alkoxycarbonyl, arylcarbonyl and heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

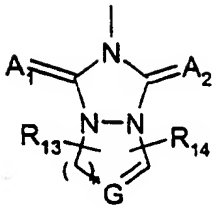
R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, nitro, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, (C_{3-6})cyclocarbonyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-6})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be optionally substituted with one or one more of the following group consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxy, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, haloaryl, alkoxyaryl, aryoxy, arylthio, haloaryloxy, heteroaryl, heteroaryloxy and (C_{3-7})cycloalkyl;

n* is represent an integer from 0 to 2;

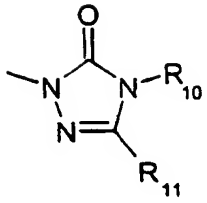
Q is selected from;



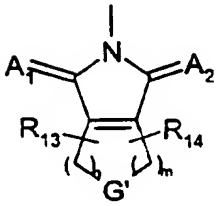
Q_1



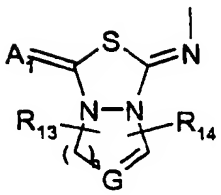
Q_2



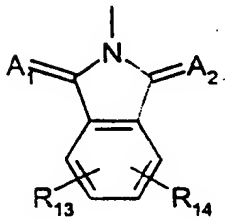
Q_3



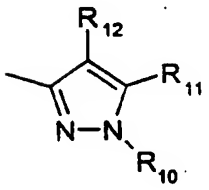
Q_4



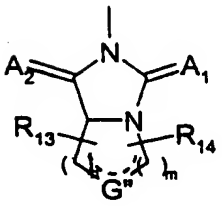
Q_5



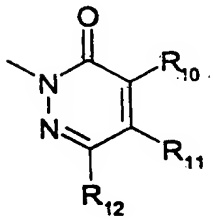
Q_6



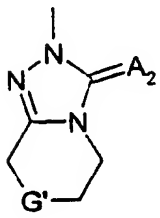
Q_7



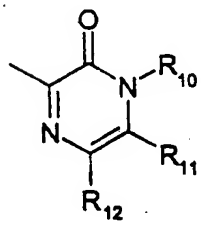
Q_8



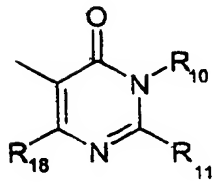
Q_9



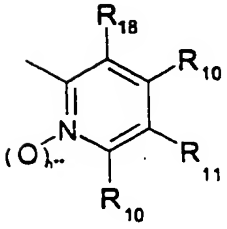
Q_{10}



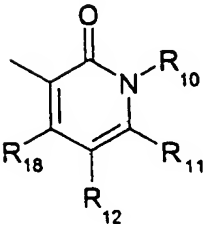
Q_{11}



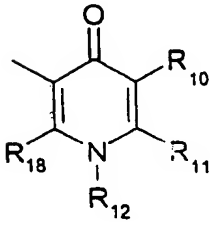
Q_{12}



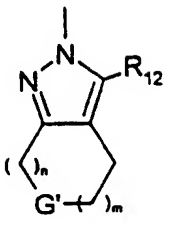
Q_{13}



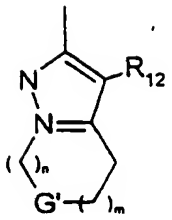
Q_{14}



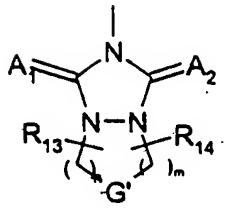
Q_{15}



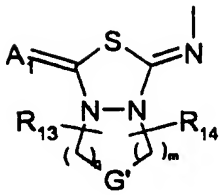
Q_{16}



Q_{17}



Q_{18}



Q_{19}

wherein

A_1 and A_2 are independently oxygen or sulfur;

R_{10} is hydrogen, halogen, cyano, nitro, formyl, (C_{1-4})alkyl, (C_{1-4})haloalkyl, amino, (C_{1-4})alkylamino, (C_{1-4})haloalkylamino, (C_{1-4})alkoxyamino, (C_{1-4})haloalkoxyamino, (C_{1-4})alkylcarbonyl, (C_{1-4})haloalkylcarbonyl, (C_{1-4})haloalkoxycarbonyl, (C_{1-4})alkylcabonylamino, (C_{1-4})haloalkylcarbonylamino, (C_{1-4})alkoxycarbonylamino, (C_{1-4})haloalkoxycarbonylamino, (C_{1-6})alkoxyalkyl, (C_{1-6})haloalkoxyalkyl, (C_{1-6})alkylthio, (C_{1-6})haloalkylthio, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, (C_{2-6})alkynyl or (C_{2-6})haloalkynyl;

R_{11}, R_{12} and R_{18} are independent of each other and may be selected from the group consisting of hydrogen, halogen, cyano, (C_{1-4})alkyl, (C_{1-4})haloalkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkoxy, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, hydroxy or amino which may be optionally substituted with (C_{1-4})alkyl and (C_{1-4})haloalkyl;

R_{13} and R_{14} are independent of each other and may be selected from the group consisting of hydrogen, halogen, (C_{1-3})alkyl, (C_{1-3})haloalkyl, hydroxy, (C_{1-3})alkoxy, (C_{1-3})haloalkoxy, cyano, nitro, amino or (C_{1-6})alkylamino;

When R_{13} and R_{14} are taken together with the atoms to which they are attached, they represent a three to seven membered substituted or unsubstituted ring optionally containing oxygen, $S(O)_n$••• or nitrogen with following optional substitutions, one to

three halogen, cyano, nitro, hydroxy, amino, carbonyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl or (C_{3-7})cycloalkyl;

G is nitrogen or CR_{16};

G' is NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$;

G'' is nitrogen, CR_{16}, NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$;

R_{15} may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl; where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

R_{16} and R_{17} are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, (C_{3-6})cyclocarbonyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl ,(C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be optionally substituted with one or one more of the following group consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})

$_6$)haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

n and m are independent of each other and represent an integer from 0 to 2; provided that m+n is 2, 3 or 4;

n** is 0 or 1;

n*** is represent an integer from 0 to 2;

When Q is Q_1, Q_3, Q_4, Q_{13}, Q_{18} or Q_{19}, structure (Ib) is excluded;

When Q is Q_7, U is CR_9, nitrogen, NR_2, C(=O), C(=S) or C(=NR_2);

2. A compound according to the claim 1 in which

X, Y are independent of each other and are represented by hydrogen, halogen or cyano;

A is oxygen, nitrogen, NR_1;

D is nitrogen or NR_2;

M is nitrogen or NR_2;

E and L are independent of each other and may be selected from CR_7, CR_8, CR_7R_8, oxygen, nitrogen, $S(O)_{n*}$, C(=O), C(=S), C(=NR_7) or CNR_7R_8;

U is oxygen, nitrogen, NR_2 or $S(O)_{n*}$;

R_1 and R_2 are independently of each other and may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{2-6})alkenyl, (C_{2-6})alkynyl, (C_{1-6})alkylcarbonyl, (C_{-6})cycloalkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, mercapto, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, haloaryl,alkoxyaryl,heteroaryl and (C_{3-7})cycloalkyl;

R_3, R_4, R_5, R_6, R_7, R_8 and R_9 are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-}

$_6$)alkylcarbonyloxy, (C_{1-6})haloalkylcarb nyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})hal alkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, aryloxy, heteroaryl heteroaryloxy and (C_{3-7})cycloalkyl;

n* is represent an integer from 0 to 2;

When Q.is Q_1 or Q_3, structure (Ib) is excluded;

When Q is Q_7, U is nitrogen or NR_2;

Q is selected from Q_1, Q_2, Q_3, Q_7, Q_9, Q_{10}, Q_{16} or Q_{17};

wherein

A_1 and A_2 are independently oxygen or sulfur;

R_{10} is (C_{1-3})alkyl, (C_{1-3})haloalkyl or amino

R_{11} and R_{12} are independent of each other and may be selected from the group consisting of hydrogen, halogen, cyano, (C_{1-4})alkyl, (C_{1-4})haloalkyl, (C_{1-4})alkoxy, (C_{1-4})haloalkoxy, (C_{2-6})alkenyl, (C_{2-6})haloalkenyl, hydroxy and amino, which may be optionally substituted with (C_{1-4})alkyl or (C_{1-4})haloalkyl;

R_{13} and R_{14} are independently of each other and may be selected from the group consisting of hydrogen, halogen, (C_{1-3})alkyl, (C_{1-3})haloalkyl, hydroxy, (C_{1-3})alkoxy, (C_{1-3})haloalkoxy, cyano, nitro, amino and (C_{1-6})alkylamino;

G is nitrogen or CR_{16};

G' is NR_{15}, oxygen, $S(O)_n$••• or $CR_{16}R_{17}$;

R_{15} may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl;

R_{16} and R_{17} are independent of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-}

$_6$)haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;
n and m are independent of each other and represent an integer from 0 to 2; provided that m+n=2 or 3;
n** is 0 or 1;
n*** is represent an integer from 0 to 2;

3. A compound according to the claim 2 in which
X,Y are independent of each other, represent hydrogen, halogen, cyano;
A and U are oxygen;
D and M are nitrogen or NR_2;
E and L are independent of each other and may be CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ or CNR_7R_8;
R_2 may be selected from the group consisting of hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})cycloalkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl and heteroarylcarbonyl;
R_7, and R_8 and are independently of each other and may be selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, cyano, (C_{1-6})alkyl, (C_{1-6})hal alkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-6})alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, (C_{1-6})alkylcarbonyl, arylcarbonyl,

(C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro,carboxy (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

A_1 and A_2 are oxygen;

When Q is Q_1 or Q_7 structure (Ib) is excluded;

Q is Q_1, Q_7 or Q_{17};

R_{10} is methyl or amino;

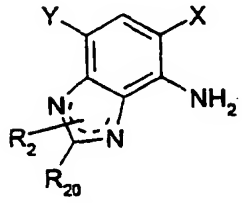
R_{11} is (C_{1-3})alkyl, (C_{1-3})haloalkyl, (C_{1-3})alkoxy or (C_{1-3})haloalkoxy;

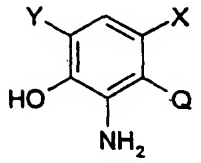
R_{12} is hydrogen, halogen or (C1-3)alkyl;

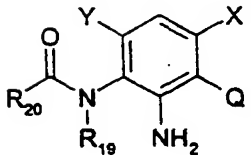
4. A compound or its salt represented by the formula a, b, c, d, e or f:

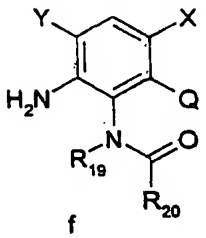

a


b


c


d


e


f

in which

X is hydrogen or halogen;

Y is halogen, cyano, nitro, (C_{1-3})haloalkyl, or (C_{1-3})haloalkoxy;

Q is O_1, Q_2, Q_3, Q_7, Q_9, Q_{10}, Q_{16} or Q_{17};

R_{19} is hydrogen, (C_{1-6})alkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})haloalkylcarbonyl, arylcarbonyl, heteroarylcarbonyl;

where any of these groups may be optionally substituted with one or more of the following groups consisting of halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

R_{20} is selected from the group consisting of hydrogen, halogen, hydroxy, mercapto, amino, cyano, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkoxy,(C_{1-6})haloalkoxy, (C_{1-}

$_6$)alkoxyalkyl, (C_{2-6})alkynyl ,(C_{2-6})alkenyl, aryl, heteroaryl, aryloxy, heteroaryloxy, (C_{3-6})cycloalkyl, carboxy, (C_{1-6})alkylcarbonyl, arylcarbonyl, (C_{1-3})haloalkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxycarbonyl , (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylthiocarbonyl, (C_{1-6})haloalkylthiocarbonyl, (C_{1-6})alkoxythiocarbonyl, (C_{1-6})haloalkoxythiocarbonyl,(C_{1-6})alkylamino, arylsulfonylamino, arylamino, (C_{1-3})alkylthio, arylthio, (C_{2-6})alkenylthio, (C_{2-6})alkynylthio, (C_{1-6})alkylsulfinyl, (C_{2-6})alkenylsulfinyl, (C_{2-6})alkynylsulfinyl, (C_{1-6})alkylsulfonyl, (C_{2-6})alkenylsulfonyl, (C_{2-6})alkynylsulfonyl, arylsulfonyl, where any of these groups may be non-substituted or substituted with any of the functional groups represented by one more of the following ; halogen, hydroxy, cyano, nitro, amino, caboxyl, (C_{1-6})alkyl, (C_{1-6})haloalkyl, (C_{1-6})alkylcarbonyl, (C_{1-6})alkylcarbonyloxy, (C_{1-6})haloalkylcarbonyl, (C_{1-6})haloalkylcarbonyloxy, (C_{1-6})alkoxy, (C_{1-6})alkoxycarbonyl, aminocarbonyl, (C_{1-6})alkylaminocarbonyl, (C_{1-6})haloalkoxy, (C_{1-6})haloalkoxycarbonyl, (C_{1-6})alkylsulfonyl, (C_{1-6})haloalkylsulfonyl, aryl, heteroaryl and (C_{3-7})cycloalkyl;

5. A method for controlling the growth of undesired plant species in plantation crops which comprises applying to the locus of the crop a herbicidally effective amount of a compound or irs salt of formula (Ia) or (Ib) of the claim 1.

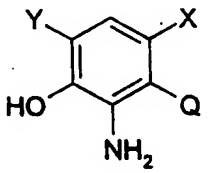
6. Herbicidal composition, characterized in that it contains at least one compound according to the claim1.

7. The herbicidal composition according to the claim 6 wherein it contains and an auxiliary agent such as the compound of formula (Ia) or (Ib) or its salt with at least one surfactant or an agricultural adjuvant, solid or liquid diluent.

8. A method for controlling undesired vegetation in a crop field such as corn or soybean by applying to the locus of the crop to be protected a herbicidally effective amount of a compound of the claim 1.

9. A method to defoliate potato and cotton using a compound of the claim 1.

10. A process for the preparation of the compound of formula (Ib) as claimed in claim 1, which comprises cyclizing a compound according to formula d



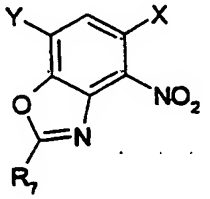
d

wherein

X, Y and Q are as previously defined, with an acid chloride, acid anhydride or acid in the presence of a cyclization catalyst in an inert solvent or diluent.

11. A process of the preparation of the intermediate of the formula VIII, which comprises reducing a compound according to formula VI

VIII

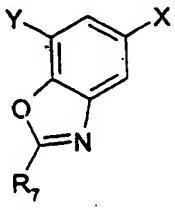


VI

wherein

X, Y and R_7 are as previously defined.

12. A process for the preparation of the intermediate of the formula VI as claimed in claim 11, which comprises nitrating a compound according to formula V

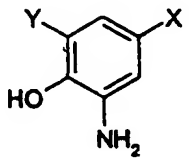


V

wherein

X, Y and R_7 are as previously defined.

13. A process for the preparati n of the intermediate of the formula V as claimed in claim 12, which comprises cyclizing a compound according to formula IV

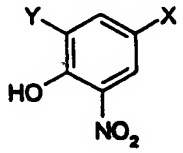


IV

wherein

X and Y are as previously defined, with an acid or acid chloride in the presence of a catalyst in an inert solvent or diluent.

14. A process for the preparation of the intermediate of the formula IV as claimed in claim 13, which comprises reducing a compound according to formula III

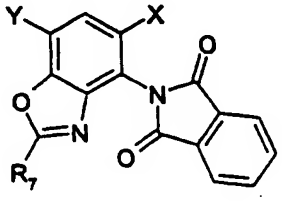


III

wherein

X and Y are as previously defined, with a reducing reagent.

15. A process for the preparation of the intermediate of the formula VIII as claimed in claim 11, which comprises deprotecting a compound according to formula XVIII

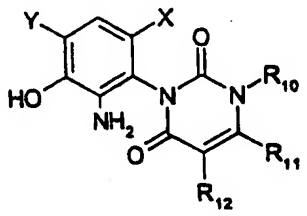


XVII

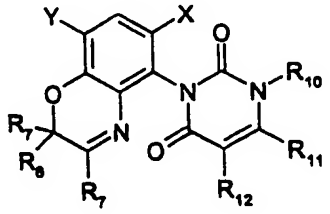
wherein

X, Y and R_7 are as previously defined.

16. A process for the preparation of the compound of the formula XXV as claimed in claim 1, which comprises cyclizing a compound according to formula XXIV



XXIV

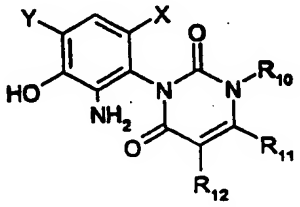


XXV

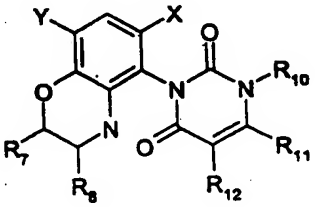
wherein

X, Y, R_7, R_8, R_{10}, R_{11} and R_{12} are as previously defined.

17. A process for the preparation of the compound of the formula XXVI as claimed in claim 1, which comprises cyclizing a compound according to formula XXIV



XXIV

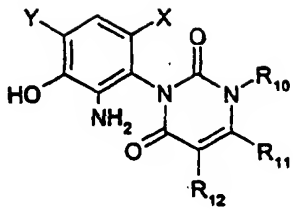


XXVI

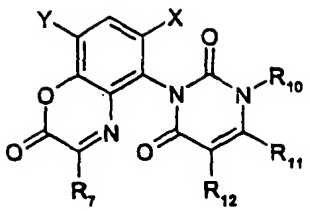
wherein

X, Y, R_7, R_8, R_{10}, R_{11} and R_{12} are as previously defined.

18. A process of the preparation of the compound of the formula XXVII as claimed in claim 1, which comprises cyclizing a compound according to formula XXIV



XXIV

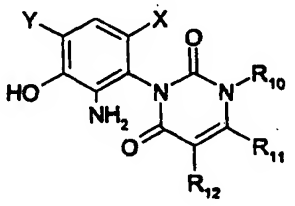


XXVII

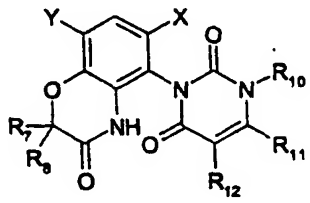
wherein

X, Y, R_7, R_{10}, R_{11} and R_{12} are as previously defined.

19. A process for the preparation of the compound of the formula XXVIII as claimed in claim 1, which comprises a cyclizing a compound according to formula XXIV.



XXIV



XXVIII

wherein

X, Y, R_7, R_8, R_{10}, R_{11} and R_{12} are as previously defined.

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98/27090	6/1998	WIPO
98/38188	9/1998	WIPO
99/06394	2/1999	WIPO
99/31091	6/1999	WIPO

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/18836

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 544/51, 105, 309, 310, 236, 356, 238; 546/119, 121; 548/159, 217, 305.1, 306.1; 504/221, 225, 243, 246, 238, 236, 267, 270, 276

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,783,521 A (RHEINHEIMER et al) 21 July 1998, col. 20, lines 19-20.	1
X - Y	US 4,881,967 A (SEMPLE) 21 November 1989, see entire document.	1-9 --- 1-9
Y	US 5,441,925 A (THEODORIDIS) 15 August 1995, see entire document.	1, 5-8
Y	US 5,416,065 A (BRUNNER et al) 16 May 1995, see entire document.	1, 4-8
Y	US 5,665,681 A (SECKINGER et al) 09 September 1997, see entire document.	1, 4-8
Y	US 5,661,108 A (CRAWFORD et al) 26 August 1997, see entire	1, 4-8

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
01 DECEMBER 1999	10 FEB 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer DEEPAK RAO Telephone No. (703) 308-1235

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/18836

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,753,595 A (CRAWFORD et al) 19 May 1998, see entire document.	1-15
Y	US 5,521,147 A (THEODORIDIS) 28 May 1996, see entire document.	1-8
Y	WO 97/08171 A1 (HEISTRACHER et al) 06 March 1997, see entire document.	1-9
Y	US 5,523,280 A (CHENE et al) 04 June 1996, see entire document.	1-8
X	US 5,082,841 A (BROWN et al) 21 January 1992, see col. 11-12, the intermediates in Example 11.	1
X	Chem. abstr., Vol. 63, No. 12, 06 December 1965 (Columbus, OH, USA) page 16340, column 2, the abstract no. 16340h, MONTGOMERY, J.A. 'Synthesis of potential anticancer agents.' J. Med. Chem. 1965, 8(6), pages 737-740.	4
X	Chem. abstr., Vol. 58, No. 1, 07 January 1963 (Columbus, OH, USA) page 879, column 1, the abstract no. 879g, EFROS, A.M. 'Action of benzimidazole derivatives on the growth and development of grain-producing plants.' Dokl. Akad. Nauk SSSR. 1962, 146, 236-237.	4
Y	US 5,712,225 A (HONG et al) 27 January 1998, see entire document.	1-9
Y	US 5,366,955 A (NAGANO et al) 22 November 1994, see entire document.	16-19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/18836

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

A01N 43/36, 43/42, 43/56, 43/58, 43/84; C07D 231/16, 237/04, 239/10, 235/04, 265/36, 263/54, 277/62

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

544/51, 105, 309, 310, 236, 356, 238; 546/119, 121; 548/159, 217, 305.1, 306.1; 504/221, 225, 243, 246, 238, 236, 267, 270, 276

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s)s 1-2 (in part), 3, 5-9 (in part) and 16-19, drawn to compounds of formula (Ia) wherein M is N, A is O or S and E & L are selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition, method of use and process of preparation.
Group II, claim(s) 1-2 and 5-9 (all in part), drawn to compounds of formula (Ia) wherein M is N, A is N and E & L are selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition and method of use.
Group III, claim(s) 1 and 5-9 (all in part), drawn to compounds of formula (Ia) wherein one of A or M is N and the other is (substituted)carbon and E & L are selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition and method of use.
Group IV, claim(s) 1 and 5-9 (all in part), drawn to compounds of formula (Ia) wherein A and M are (substituted)carbon and E & L are selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition and method of use.
Group V, claim(s) 1 and 5-9 (all in part), drawn to compounds of formula (Ib) other than those of Groups I-IV, corresponding composition and method of use.
Group VI, claim(s)s 1-2 (in part), 3, 5-9 (in part) and 10-15, drawn to compounds of formula (Ib) wherein D is N, U is O or S and E is selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition, method of use and process of preparation.
Group VII, claim(s) 1-2 and 5-9 (all in part), drawn to compounds of formula (Ib) wherein D and U are N and E is selected from CR_7, CR_8, CR_7R_8, C(=O), C(=S), $C(=NR_7)$ and CNR_7R_8, corresponding composition and method of use.
Group VIII, claim(s) 1 and 5-9 (all in part), drawn to compounds of formula (Ib) other than those of Groups I-IV, corresponding composition and method of use.
Group IX, claim(s) 4 (in part), drawn to compounds of formulae a, b or c.
Group X, claim(s) 4 (in part), drawn to compounds of formula d, e or f.

The inventions listed as Groups I-X do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the variable core created by various definitions of A, E, L, M and Q in the compounds of formulae (Ia) and (Ib) do not belong to a recognized class of chemical compounds in the art. Groups IX-X and I, VI are related in a intermediate and final product relationship, however, the intermediates and final products lack the same essential structural elements.